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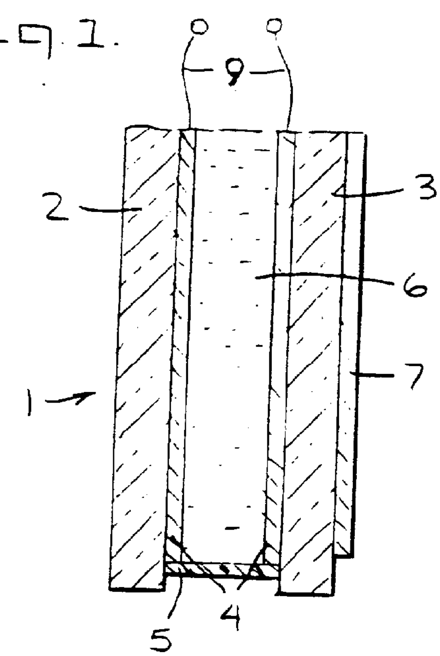
(54) **Electrochemichromic solutions, processes for preparing and using the same, and devices manufactured with the same.**

(57) The present invention relates to electrochromic solutions and devices manufactured therefrom. More precisely, the present invention relates to electrochemichromic compounds and processes for preparing the same. The present invention also relates to electrochemichromic solutions of such compounds, and those devices manufactured with the same, that demonstrate superior responsiveness to those solutions known heretofore when an applied potential is introduced thereto. And, these solutions, when contained within electrochemichromic devices, demonstrate ultraviolet stability, thermal stability and cycle stability. The responsiveness observed in terms of solution coloring with respect to the solutions, and devices containing the same, of the present invention is of a greater rapidity, intensity and uniformity than those electrochemichromic solutions of the prior art. Preparation of these solutions involve the novel process of pre-treating at least one of the electrochemichromic compounds with a redox agent prior to placing it in contact with the other electrochemichromic compound. Moreover, the present invention relates to methods of preparing such novel solutions and processes for using these solutions to provide devices that exhibit and benefit from the aforementioned superior characteristics.

Fig. 1.



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BACKGROUND OF THE INVENTION

Technical Field of the Invention

The present invention relates to electrochromic solutions and devices manufactured therefrom. More particularly, the present invention relates to electrochemichromic compounds and processes for preparing the same. The present invention also relates to electrochemichromic solutions of such compounds, and devices using the same, that demonstrate superior responsiveness to those solutions known heretofore when an applied potential is introduced thereto. That is, the responsiveness observed, in terms of solution coloring, is of a greater rapidity, intensity and uniformity than those prior art electrochemichromic solutions. These solutions also demonstrate ultraviolet stability, thermal stability and cycle stability. In addition, the present invention relates to processes for preparing such novel solutions and processes for using these solutions to manufacture devices that exhibit the aforementioned superior characteristics and accordingly benefit therefrom.

Brief Description of the Prior Art

Such solutions, and the devices manufactured employing the same, are known [see, e.g. United States Patents 3,806,229 (Schoot), 3,280,701 (Donnelly), 3,451,741 (Manos), 4,902,108 (Byker I), 5,128,799 (Byker 11) and 5,140,455 (Varaprasad), commonly assigned co-pending United States patent applications Ser. Nos. 07/456,164 (filed December 22, 1989), 07/458,969 (filed December 29, 1989) and 07/756,342 (filed September 6, 1991), and I.V. Shelepin, Electrokhimya, 13(3), 404-08 (March 1977)].

Typically, in the context of such devices, anodic compounds and cathodic compounds are placed together in a solvent to form a solution which is then placed within a cell housed by the device. When an applied potential is introduced to the device, the solution contained within colors thereby reducing the amount of light that is transmitted therethrough.

Although prior endeavors have proven satisfactory, an improvement in the rapidity, intensity and uniformity of the solution coloring would be advantageous inasmuch as the amount of light transmitted therethrough would further be decreased and the glare resulting from the face of those devices housing the solutions would also be decreased. Such an event, combined with improvements to the ultraviolet stability, thermal stability and cycle stability, would benefit those commercial applications currently employing solutions of this nature and would create new opportunities for commercial activity.

Thus, it would be desirable for an electrochemichromic solution to demonstrate an enhanced rapidity, intensity and uniformity of solution coloring when the solution is influenced by the introduction of an applied potential thereto. It would also be desirable to provide a process for preparing these solutions. It would further be desirable to provide a process for using these solutions. Finally, it would be desirable to provide a device manufactured with the electrochemichromic solutions of the present invention that benefits from the above-noted advantages of these solutions when employed therewith.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide novel electrochemichromic compounds and processes for preparing these compounds.

It is also an object of the present invention to provide electrochemichromic solutions from those compounds that demonstrate enhanced rapidity, intensity and uniformity of solution coloring when the solution is influenced by the introduction of an applied potential thereto.

It is a further object of the present invention to provide processes for preparing these solutions.

It is a still further object of the present invention to provide processes for using these solutions.

It is another object of the present invention to provide devices manufactured with the electrochemichromic solutions of the present invention that benefit from the advantages provided by these solutions when employed therewith. And, it is yet another object of the present invention to provide such solutions that, when employed in these devices, demonstrate ultraviolet stability, thermal stability and cycle stability.

The present invention solves the aforementioned shortcomings of the prior art by providing for the first time electrochemichromic compounds, and electrochemichromic solutions of these compounds, that are capable of demonstrating enhanced rapidity, intensity and uniformity of solution coloring while demonstrating ultraviolet stability, thermal stability and cycle stability. Preparation of these compounds and solutions involve the process of pre-treating an electrochemichromic compound with a redox agent prior to use.

More specifically, the electrochemichromic solutions of this invention are comprised of an anodic compound -- having been previously contacted with a redox agent to alter its valence state --, which anodic com-

pound may be combined with anodic compound(s) that do not require such a redox pre-treatment to render them useful in this connection, a cathodic compound and a solvent such that the redox potential of the anodic compound in an altered valence state is greater than the redox potential of the cathodic compound while each of these compounds is contacted with that solvent. In addition, ultraviolet stabilizing agents and electrolytic materials and the like may be optionally added thereto to modify the physical characteristics of these solutions.

The process for preparing these solutions comprises solubilizing the anodic compound in a solvent; contacting this solubilized anodic compound with a redox agent to alter its valence state; removing that amount (if any) of redox agent that has remained unreacted; introducing a cathodic compound to the solution containing the anodic compound having a valence state different to that when it was initially placed in solution; and introducing an applied potential to this solution to cause coloring thereof. Optionally, after removing any unreacted redox agent from the solution of anodic compound, that anodic compound may be isolated prior to subsequently combining it with a cathodic compound.

It is to be understood that the anodic compound as defined herein is prepared by solubilizing an electrochemichromic compound in a solvent and contacting this solubilized electrochemichromic compound with a redox agent to alter the valence state of the electrochemichromic compound in such a way that an anodic compound is created in the solution. This anodic compound is characterized by the fact that it has a different valence state than the solubilized electrochemichromic compound possessed prior to having been contacted with the redox agent. This anodic compound may be left to remain in solution or isolated therefrom, and employed thereafter in conjunction with a cathodic compound to form an electrochemichromic solution.

It is the initial pre-treatment of the anodic compound, which alters its valence state and its redox potential such that the pre-treated anodic compound bears a more positive redox potential than the cathodic compound with which it is to be placed in solution, where the point of novelty of the present invention lies.

Capitalizing on this, the electrochemichromic solutions of the present invention, and the processes for preparing and using the same, show utility in the manufacture of devices containing the solutions. The devices so manufactured benefit from the enhanced coloring capability of these solutions which not only affects the amount of light transmitted therethrough, but also the extent to which glare is reflected from such devices. This enhanced coloring capability may be continuously varied by controlling the magnitude, duration and polarity of the applied potential introduced thereto. Examples of such devices are mirrors -- e.g., vehicular, architectural or specialty mirrors, such as those useful in periscopic or dental applications --, glazings -- e.g., architectural, aeronautical or vehicular glazings, like windows, sun roofs, sun visors or shade bands --, privacy or security partitions, information displays, optically attenuating contrast filters, lenses and the like.

Thus, the present invention exemplifies a further advance in the art that will become readily apparent and more greatly appreciated by a study of the detailed description taken in conjunction with the drawings which follow hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts a sectional view of an electrochemichromic cell housing an electrochemichromic solution according to the present invention.

Figure 2 depicts a perspective view of an electrochemichromic mirror assembly -- i.e., an interior rearview automobile mirror -- according to the present invention.

The depictions in these figures are for illustrative purposes and thus are not drawn to scale.

DETAILED DESCRIPTION OF THE INVENTION

In order to fully appreciate the teaching of the present invention, the following terms are defined herein. These terms and expressions employed herein are used as terms of expression only and are not meant to be construed to limit the instant teaching.

"Anodic Compound" -- is meant to refer to a compound capable of undergoing a reversible color change when its valence state is altered due to oxidation. Unless otherwise specifically noted herein, reference to "anodic compound" is meant to include anodic compounds that have been generated by initially pre-treating an electrochemichromic compound with a redox agent, and combinations of such resulting anodic compounds with anodic compounds that do not require such a redox pre-treatment to render them useful in this connection.

"Bleaching" -- is meant to refer to the affirmative steps of either (1) removing the applied potential, (2) applying zero potential or (3) momentarily reversing the polarity of the applied potential before performing either steps (1) or (2) so as to cause electrochemichromic compounds to revert back to their respective substantially colorless valence states.

"Cathodic Compound" -- is meant to refer to a compound capable of undergoing reversible color change

when its valence state is altered due to reduction.

"Color" or "Coloring" -- is meant to refer to the ability of an electrochemichromic solution to decrease the amount of light transmitted therethrough thereby causing a color to form that is different than the color, or the lack of color, initially present in the solution. Thus, coloring may refer to color formation from an initially substantially colorless state or color change from one initially colored state to a substantially different colored state. It is of course to be understood that different anodic compounds and cathodic compounds, individually or in combination, may generate different color spectrums in the context of the present invention when their respective valence states are altered by an applied potential which is introduced to a solution containing those compounds.

"Electrochemichromic Compound" -- is meant to refer to either an anodic compound or a cathodic compound, as defined hereinabove.

"Electrochemichromic Solution" -- is meant to refer to a solution comprising at least one electrochemichromic compound.

"Iris effect" -- is meant to refer to the observation of non-uniform coloring or bleaching of an electrochemichromic solution when an applied potential is introduced to a cell housing that solution. This effect is typically due to the potential drop across the surface of the transparent conductive coatings present on the surfaces of the substrates of the electrochemichromic cell which results in the applied potential being highest adjacent to the bus bar and lowest at the center of this cell as the electrical current passes through the solution. Accordingly, it is not surprising that the solution will typically display non-uniform coloring by initially coloring the perimeter of the cell where the bus bars are located -- i.e., closest to the point where the applied potential comes in contact with the electrochemichromic solution -- and thereafter coloring toward the center of the cell.

"Redox Agent" -- is meant to refer to any material, or means, capable of altering the valence state of an electrochemichromic compound -- e.g., a reducing agent or an oxidizing agent -- that has a compatible redox potential to that electrochemichromic compound being acted upon. More specifically, when the redox agent is a reducing agent, this agent should possess a lower redox potential than that of the compound being reduced thereby driving the reduction process. Contrariwise, when the redox agent is an oxidizing agent, this agent should possess a higher redox potential than that of the compound being oxidized thereby driving the oxidation process. Regarding a means for altering the valence state of an electrochemichromic compound, an electrochemical means is suitable.

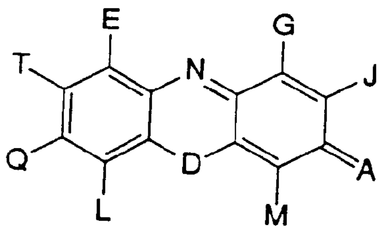
"Response Time" -- is meant to refer to that period of time required for the electrochemichromic compound present in solution to change initially from a valence state that is substantially colorless to a valence state bearing color, or vice versa (see Bleaching). Alternatively, this time may refer to that period of time required for an electrochemichromic compound to change from a valence state bearing one color to a valence state bearing a substantially different color. This period of time will often vary depending on the specific physical characteristics and concentrations of the constituents present in the electrochemichromic solution and the operating conditions and physical construction of the electrochemichromic system. In addition, the response time may not be, and often is not, the same for the reverse processes of solution coloring and solution bleaching.

"Valence State" -- is meant to refer to a state of oxidation or reduction of a given electrochemichromic compound. In that regard, an altered valence state is merely an alteration in valence state. That is, the gain of one or more electrons (reduction) will lower the valence state whereas the loss of one or more electrons (oxidation) will raise the valence state of the electrochemichromic compound.

"Self-erasing" -- is meant to refer to the substantially spontaneous fading of solution color -- i.e., an increase of light transmittance -- when the applied potential is removed from the solution. This feature is provided by the spontaneous reactions of oxidized anodic compounds with reduced cathodic compounds to afford anodic compounds and cathodic compounds in their respective valence states -- i.e., those valence states which display the least, or substantially no, color.

In accordance with the teaching of the present invention, the anodic compound and the cathodic compound may each comprise one or more individual electrochemichromic compounds. Further, while the number of individual electrochemichromic compounds comprising the anodic compound is independent of the number of individual electrochemichromic compounds comprising the cathodic compound, that is not to say that the anodic compound and the cathodic compound may not comprise the same number of different individual electrochemichromic compounds. Rather, it merely indicates that the number of different individual electrochemichromic compounds comprising either the anodic compound or the cathodic compound does not depend on the identity of those individual electrochemichromic compounds chosen.

With this in mind, the anodic compound, prior to contacting with a redox agent, may be selected from the class of chemical compounds represented by the following formula



I

wherein A is O, S or NRR_1;

wherein R and R_1 may be the same or different, and each may be selected from the group consisting of H or any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms, such as CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$ and the like; provided that when A is NRR_1, Q is H, OH or NRR_1; further provided that when A is NRR_1, a salt may be associated therewith; still further provided that when both A and Q are NRR_1, A and Q need not, but may, be the same functional group;

D is O, S, NR_1 or Se;

E is R_1, COOH or $CONH_2$; or, E and T, when taken together, represent an aromatic ring structure having six ring carbon atoms when viewed in conjunction with the ring carbon atoms to which they are attached;

G is H;

J is H, any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms, such as CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$ and the like, NRR_1,

$$NR\underset{\underset{O}{\|}}{C}R_1,$$

OR_1, phenyl, 2,4-dihydroxyphenyl or any halogen; or, G and J, when taken together, represent an aromatic ring structure having six ring carbon atoms when viewed in conjunction with the ring carbon atoms to which they are attached;

L is H or OH;

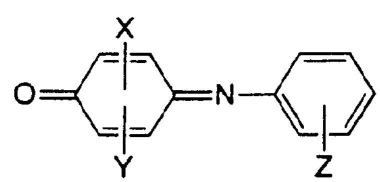
M is H or any halogen;

T is R_1, phenyl or 2,4-dihydroxyphenyl; and

Q is H, OH or NRR_1, provided that when L and Q are OH, L and Q may also be any salt thereof.

Those salts include, but are not limited to, alkali metal salts, such as lithium, sodium, potassium and the like. In addition, when A is NRR_1, tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-), trifluoromethane sulfonate ($CF_3SO_3^-$), hexafluorophosphate (PF_6^-), acetate (Ac^-) and any halogen may be associated therewith. Moreover, the ring nitrogen atom in this chemical formula may also appear as an N-oxide.

Alternatively, the anodic compound, prior to contacting with a redox agent, may be selected from the class of chemical compounds represented by the following formula

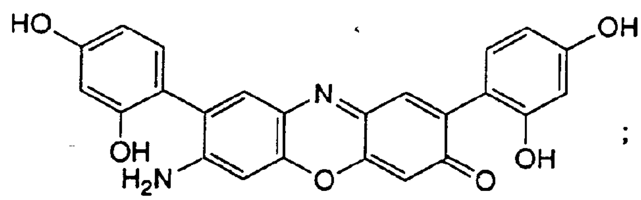


II

wherein X and Y may be the same or different, and each may be selected from the group consisting of H, any halogen or NRR_1, wherein R and R_1 may be the same or different, and each may be selected from the group consisting of H, any alkyl straight- or branched-chained alkyl constituent having from about one carbon atom to about three carbon atoms; or, X and Y, when taken together, represent an aromatic ring structure having

six ring carbon atoms when viewed in conjunction with the ring carbon atoms to which they are attached; and Z is OH or NRR_1, or salts thereof.

Preferably, the anodic compound represented by formula I, prior to contacting with a redox agent, may be selected from the group consisting of the class of chemical compounds represented by the following formulae



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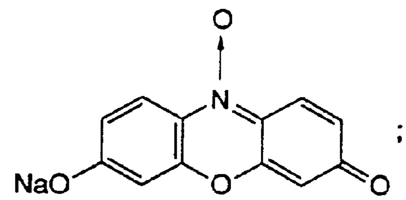
III
Lacmoid (NH_2)



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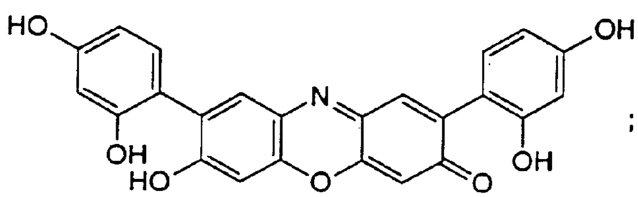
IV
Resazurin



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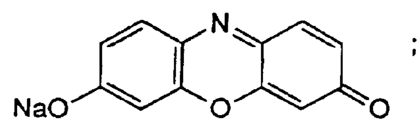
V
Lacmoid (OH)



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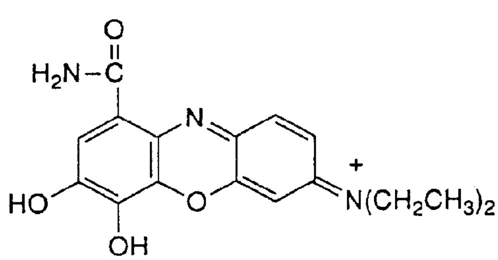
VI
Resorufin



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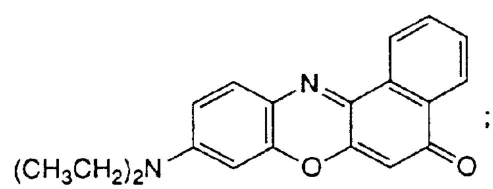
VII
Celestine Blue



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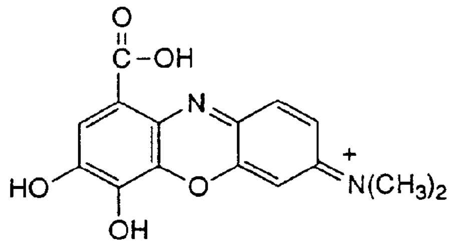
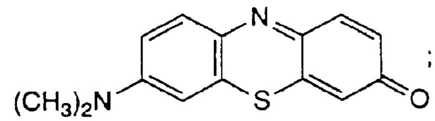
VIII
Nile Red



IX
Gallocyanine

;



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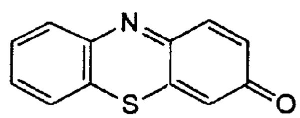
X
methylene violet
(Bernthsen)
(MVTB)



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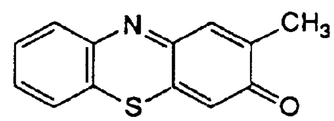
XI
phenothiazin-3-one
(PT)



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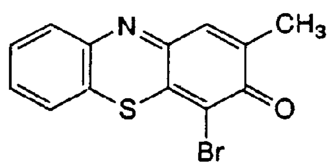
XII
2-methyl-phenothiazin-3-one
(MPT)



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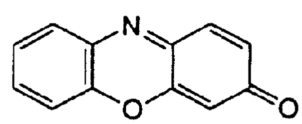
XIII
2-methyl-4-bromo-
phenothiazin-3-one
(BMPT)



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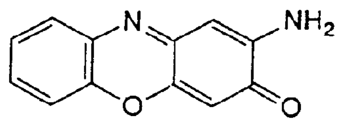
XIV
phenoxazin-3-one
(POZ)



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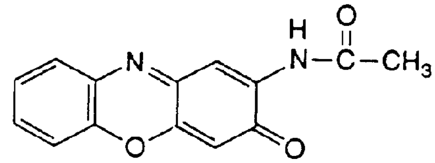
XV
2-amino-phenoxazin-3-one
(APOZ)



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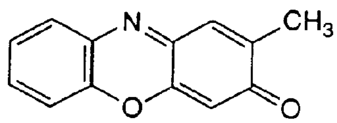
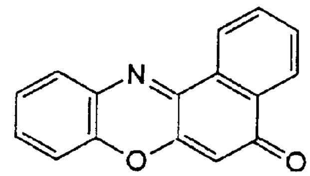
XVI
2-acetylamino-phenoxazin-3-one
(AAPOZ)



;

XVII
2-methyl-phenoxazin-3-one
(MPOZ)



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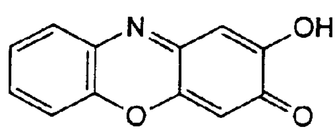
XVIII
1,2-benzo-phenoxazin-3-one
(BPOZ)



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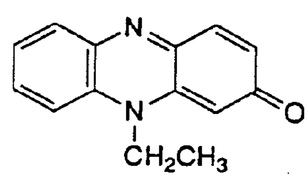
XIX
2-hydroxy-phenoxazin-3-one
(HPOZ)



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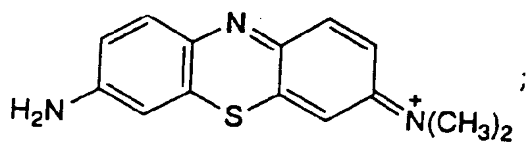
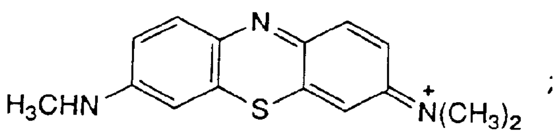
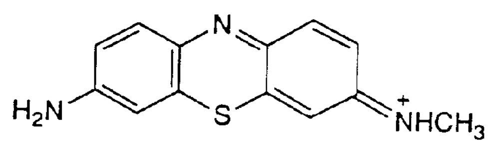
XX
2-keto-N-ethyl-phenazine
(KEPA)



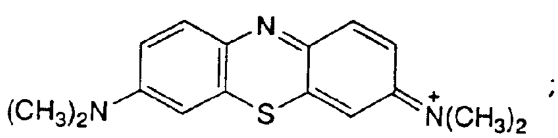
XXI
Azure A
(AA)



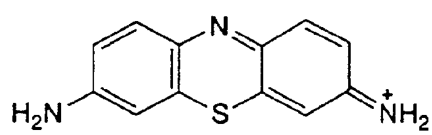
XXII
Azure B
(AB)



XXIII
Azure C
(AC)



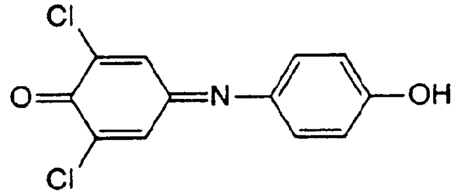
XXIV
Methylene Blue
(MB)



XXV
Thionin
(TH)

and combinations thereof.

In addition, a preferred anodic compound represented by formula II, prior to contacting with a redox agent, includes but is not limited to



XXVI
2,6-dichloro-indophenol
(DCI)

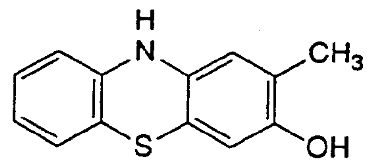
and salts thereof.

Especially preferred anodic compounds, prior to contacting with a redox agent, are MVTB (X), MPT (XII), PT (XI) and POZ (XIV).

Most preferably, the anodic compounds, prior to contacting with a redox agent, are MVTB (X) and MPT

(XII).

While the anodic compounds that are prepared according to the present invention may be left to remain in solution and thereafter conbined with a cathodic compound, those anodic compounds may also be isolated from the solution prior to such combination. A preferred anodic compound of this nature is MPT, which may be reduced according to this invention and thereafter isolated as a white precipitate prior to combining it with a cathodic compound in solution. It is believed that this reduced MPT ("RMPT") [XII(a)] is 2-methyl-3-hydroxyphenothiazine represented by the following chemical formula

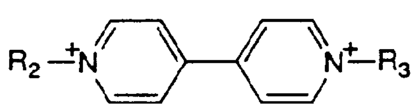


XII(a)
(RMPT)

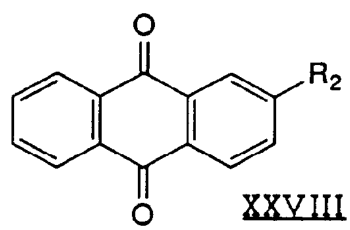
For a further description of a reduction and isolation procedure, see Example 19(A), infra.

Moreover, any one or more of the anodic compounds represented by the structures of chemical formulae I or II, or combinations thereof, may be advantageously combined, after having been contacted with a redox agent, in any proportion with other anodic compounds that need not be pre-contacted with a redox agent as taught herein, such as 5,10-dihydro-5,10-dimethylphenazine ("DMPA"), to achieve the results so stated herein. In addition to these results, colorimetric distinct changes from those colors displayed by electrochemichromic solutions of individual anodic compounds may be witnessed when such combinations are employed in the electrochemichromic solutions of the present invention. Preferred among these possible combinations are combinations of RMPT [XII(a)] (reduced according to the present invention) and DMPA. Such combinations (of the electrochemichromic compounds of the present invention represented by the structures of chemical formulae I or II with anodic compounds that need not be pre-contacted with a redox agent as taught herein, such as DMPA) may vary in proportions from about 99:1 (mole/mole) to about 1:99 (mole/mole), with about 2:1 (mole/mole) RMPT [XII(a)] to DMPA being preferred.

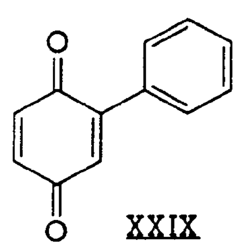
A choice of a cathodic compound should also be made. The cathodic compound may be selected from the class of chemical compounds represented by the following formulae



XXVII $2x^-$;



XXVIII ;



XXIX

wherein R_2 and R_3 may be the same or different, and each may be selected from the group consisting of H, any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms,

or any straight- or branched-chain alkyl- or alkoxy-phenyl, wherein the alkyl or alkoxy constituent contains from about one carbon atom to about six carbon atoms; and

X is selected from the group consisting of BF_4^-, ClO_4^-, $CF_3SO_3^-$, PF_6^-, Ac^-, any halide and combinations thereof.

Preferably, R_2 and R_3 in these chemical formulae which represent the cathodic compound are each CH_2CH_3. Thus, when X is ClO_4^-, a preferred cathodic compound is ethylviologen perchlorate ($EVClO_4$).

The redox agent that is employed in the present invention to pre-treat the anodic compound may be chosen from a host of materials that demonstrate the ability to alter the valence state of such an anodic compound. While not intending to be bound by theory, the redox agent should possess a compatible redox potential to that electrochemichromic compound with which it is to be placed in contact. Although the redox agents may be in any physical form -- i.e., a solid, liquid or gaseous state --, a solid redox agent is typically preferred because of its ease of handling and use. Moreover, solid redox agents having a fine particle size -- e.g., about 50 mesh to about 400 mesh -- are also preferred because of the larger surface area provided. Alternatively, when in the gaseous state, the redox agent may advantageously be passed through a solution of an anodic compound by, for example, bubbling the gaseous redox agent through an airstone disperser.

When the chosen redox agent is a reducing agent, suitable materials that are representative candidates for use therefor may be drawn from the following non-exhaustive recitation including zinc, ascorbic acid, sodium hydrosulfite, vanadium (III) chloride, chromium (II) acetate, sulfur dioxide and any combination thereof. Preferred among these reducing agents, however, is zinc. When an electrochemical means is chosen as the reducing agent, a conventional electrochemical apparatus capable of providing a negative electrochemical potential may be used.

The redox agent for use in the instant invention may also be an oxidizing agent. In such a case, suitable materials include, but are not limited to, air, oxygen, sodium persulfate, MVTB (X), PT (XI), MPT (XII), BMPT (XIII), POZ (XIV), APOZ (XV), AAPOZ (XVI), MPOZ (XVII), BPOZ (XVIII), HPOZ (XIX), KEPA (XX), AA (XXI), AB (XXII), AC (XXIII), MB (XXIV), TH (XXV), DCI(XXVI), reduced cathodic compounds such as XXVII, XXVIII or XXIX, or combinations thereof. Also, when an electrochemical means is chosen as the oxidizing agent, a conventional electrochemical apparatus capable of providing a positive electrical potential may be used.

The solvent of choice for solubilizing the aforementioned anodic compounds and cathodic compounds should remain substantially inert to those compounds, as well as to any other constituent initially present in the electrochemichromic solution, or formed as a by-product thereafter, so as not to interfere with the electrochemical reactions occurring with respect to those electrochemichromic compounds. To that end, the solvent chosen should be capable of solubilizing those anodic compounds and those cathodic compounds while each is in its ground valence state as well as when each is in its altered valence state, or for that matter, when the two electrochemichromic compounds are not in the same valence state -- i.e., ground valence state, a high energy valence state or different high energy valence states. Thus, the different levels of solubility for different electrochemichromic compounds present in different valence states should be considered when choosing a solvent for the solutions of the subject invention. Further, the solvent should remain homogenous while preparing, using and storing the electrochemichromic solutions. Put another way, the solvent chosen should not encourage the constituents of the electrochemichromic solutions, or by-products thereof, to salt-out or precipitate from the solution, for such an event would interfere with the appearance and the effectiveness of the electrochemichromic cell and is thus obviously disadvantageous.

In another aspect of the present invention, different solvents among those described herein as suitable for use in those electrochemichromic solutions will influence shades or tints of colors to form from the same pair of electrochemichromic compounds when an applied potential is introduced thereto.

In view of the above, any solvent that remains in its liquid form over the range of temperatures that the devices manufactured with the electrochemichromic solutions of the present invention will likely be subjected to is suitable for use as a solvent herein [for a non-exhaustive recitation of suitable materials, see, e.g. commonly assigned copending United States patent applications Ser. Nos. 07/456,164 (filed December 22, 1989) and 07/458,969 (filed December 29, 1989)]. Practically speaking, however, those solvents should be stable to electrolysis and other phenomena likely to be encountered during the practice of this invention.

Although any of those solvents identified above are suitable, preferable solvents may be selected from acetonitrile, 3-hydroxypropionitrile, methoxypropionitrile, 3-ethoxypropionitrile, 2-acetylbutyrolactone, propylene carbonate, cyanoethyl sucrose, γ-butyrolactone, 2-methylglutaronitrile, N,N′-dimethylformamide, 3-methylsulfolane, glutaronitrile, 3,3′-oxydipropionitrile, methylethyl ketone, cyclopentanone, cyclohexanone, benzoyl acetone, 4-hydroxy-4-methyl-2-pentanone, acetophenone, 2-methoxyethyl ether, triethylene glycol dimethyl ether and any combination thereof. Particularly preferred solvents among that group are the combination of 3-ethoxypropionitrile with 2-acetylbutyrolactone in about 50:50, 75:25 and 80:20 ratios (v/v) and the combination of 3-ethoxypropionitrile with 2-acetylbutyrolactone and cyanoethyl sucrose in about a 55:15:30 ratio

(v/v).

Additional particularly preferred solvents include, but are not limited to, solvents comprising a combination of propylene carbonate and glacial acetic acid, a combination of 3-hydroxypropionitrile and glacial acetic acid, a combination of glutaronitrile and glacial acetic acid, a combination of 3,3′-oxydipropionitrile and glacial acetic acid, a combination of 3-methylsulfolane and glacial acetic acid, a combination of propylene carbonate, cyanoethyl sucrose and glacial acetic acid and the like. Specifically, those solvents include the combinations of 3-hydroxypropionitrile with glutaronitrile and glacial acetic acid in about 74:25:1 and 49.5:49.5:1 ratios (v/v), the combination of 3-hydroxypropionitrile with 3,3′-oxydipropionitrile and glacial acetic acid in about a 69:30:1 ratio (v/v), the combinations of propylene carbonate with glacial acetic acid in about 99.5:0.5, 99:1, 98:2 and 97:3 ratios (v/v), the combinations of propylene carbonate with cyanoethyl sucrose and glacial acetic acid in about 74:25:1 and 64:35:1 ratios (v/v) and the like. Most preferred among these herein disclosed solvents is the combination of propylene carbonate with glacial acetic acid in about 99:1 to about 97:3 ratios (v/v). And, the glacial acetic acid or acidic solvent component may be added while the combination is being prepared as a percentage of the total volume of that solvent.

To that end, it is believed that such acidic solvents not only catalyze the initial pre-treatment reaction -- i.e., the reaction between the redox agent and the anodic compound -- but may also assist in keeping the pretreated anodic compound, in its altered valence state, from acting as a redox agent toward the cathodic compound when the two electrochemichromic compounds are combined in solution at the outset. In the event that a cathodic compound possesses a more negative redox potential than that of the anodic compound, these compounds may be employed in the absence of an acidic solvent.

Notwithstanding this event, in addition to glacial acetic acid, almost any acidic solvent component, such as hydrogen halide gases in solution, perchloric acid, 2-acetylbutyrolactone, 3-hydroxypropionitrile and any combination thereof, may suffice provided that it is substantially anhydrous and further provided that it is chemically and electrochemically inert toward the electrochemichromic compounds engaged in the present invention. In one alternative, acidic solvents such as weak organic acids, like citric acid solutions and benzoic acid solutions, may be added to otherwise nonacidic solvents to render those solvents acidic. In another alternative, Lewis acids, such as boron trifluoride and the like, may also be advantageously employed. Preferably, however, glacial acetic acid should be employed. For a further recitation of suitable acidic solvents, see, e.g. Lange's Handbook of Chemistry, table 5-8, J.A. Dean, ed., 13th ed., McGraw-Hill Co., New York (1985). In general, the solvent may be selected with an eye toward having the anodic compound, bearing an altered valence state, possess a greater redox potential than that of the cathodic compound while each is in solution.

The acidic strength of the solvent should be sufficient to bring the redox potential of the anodic compound to a more positive value than that of the cathodic compound. Where at least a binary solvent is employed, the amount of the more acidic solvent component chosen should be in the range of about 0.01% (v/v) to about 75% (v/v). However, when glacial acetic acid is chosen as the acidic solvent component, about 0.5% (v/v) to about 5% (v/v) is preferred. It is worth noting, that a higher acidic strength of the solvent in the electrochemichromic solution may cause a different solution coloring spectrum or, for that matter, a different degree of intensity of the color so formed.

In addition to altering the valence state of the anodic compound by means of a redox agent, preferably in the presence of an acidic solvent, electrochemical means may also be employed to accomplish this objective. This electrochemical reaction may be performed, both with and without the presence of an acidic solvent component, employing a conventional multi-compartment electrochemical cell equipped with a working electrode, such as a platinum electrode or the like.

Other components may :also be added to the subject electrochemichromic solutions including, but not limited to, an ultraviolet stabilizing agent, an electrolytic material and any combination thereof. Because many electrochemichromic compounds, particularly anodic compounds, show a substantial ultraviolet absorbance in the ultraviolet region from about 250 nm to about 350 nm, it is often desirable to shield the electrochemichromic compounds from ultraviolet radiation. Thus, by introducing an ultraviolet stabilizing agent to the subject solution, or a solvent which acts as an ultraviolet absorber, the lifetime of the electrochemichromic solution may be extended.

Although any material known to absorb ultraviolet radiation, and thereby prevent or retard the ultraviolet degradation of the constituents presently in solution, may be employed to achieve the desired stabilizing result, provided that it is inert to those constituents and stable over the conditions of operation of the subject electrochemichromic solutions, an ultraviolet stabilizing agent, such as "UVINUL 400" [2,4-dihydroxy-benzophenone (manufactured by BASF Wyndotte Corp., Wyandotte, Michigan)], "UVINUL D-49" [2,2′-dihydroxy-4,4′-dimethoxy-benzophenone (manufactured by BASF Wyandotte Corp., Wyandotte, Michigan)], "UVINUL N-539" [2-ethyl-hexyl-2-cyano-3,3′-diphenyl-acrylate (manufactured by BASF Wyandotte Corp., Wyandotte, Michigan)], "TINUVIN P" [2-(2H-benzotriazole-2-yl)-4-methylphenyl (manufactured by Ciba Geigy Corp., Haw-

thorne, New York)], "TINUVIN 327" [2-(3′,5′-di-t-butyl-2′-hydroxyphenyl)-5-chloro-benzotriazole (manufactured by Ciba Geigy Corp., Hawthorne, New York)], "TINUVIN 328" [2 - (3′ , 5′ -di-n-pentyl-2′ -hydroxyphenyl)-benzotriazole (manufactured by Ciba Geigy Corp., Hawthorne, New York)], "CYASORB UV 24" [2,2′ -dihydroxy-4-methoxy-benzophenone (manufactured by American Cyanamide Co., Wayne, New Jersey)], acrylate or other conventional acrylate deviatives, benzotriazole or conventional benzotriazole derivatives, benzophenone or conventional benzophenone derivatives, or many sterically hindered amine complexes known in the art and combinations thereof, is preferred. In fact, "UVINUL 400" is a most preferred ultraviolet stabilizing agent and it may be advantageously used in the range of about 0.1% (w/v) to about 15% (w/v), with about 5% (w/v) to about 12% (w/v) being preferred.

An electrolytic material may also be employed in the electrochemichromic solutions to assist or enhance the conductivity of the electrical current passing therethrough, and particularly when no electrochemichromic compound of the electrochemichromic solution or any other solution component exists in an ionic state. That material may be selected from a host of known materials inert to the constituents and stable over the conditions of operation of the subject solutions. Preferred electrolytic materials include tetraethylammonium perchlorate, tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, tetrabutylammonium trifluoromethane sulfonate and any combination thereof, with tetrabutylammonium hexafluorophosphate and tetraethylammonium perchlorate being most preferred. Although impractical to specify absolute ranges for all possible electrolytic materials within the scope of this invention, if tetrabutylammonium hexafluorophosphate is chosen as the electrolytic material, a concentration of about equimolar to about five times the concentration of the electrochemichromic compounds is preferred.

Again, without intending to be bound by theory, an understanding of the triggering events which make this invention operational is instructive in the context of a preferred embodiment for preparing these electrochemichromic solutions and in a device manufactured with the same. In this connection, an anodic compound, such as MVTB (X), MPT (XII), PT (XI) and POZ (XIV), initially provided in a higher valence state than compared with the valence state that it will reach when contacted with a redox agent may be dissolved in any of the solvents identified herein, such as the combination of 3-ethoxypropionitrile with 2-acetylbutyrolactone in about an 80:20 ratio (v/v), so that a colored solution of that compound is formed.

The resulting solution may then be contacted with a redox agent, particularly a reducing agent, such as zinc, so that the anodic compound is reduced to a lower valence state and to a less colored form in solution. This reduction causes the anodic compound to gain at least one electron thereby causing the now reduced anodic compound-containing solution to lose substantially all of its color.

The preferred redox agent should be substantially insoluble in the preferred solvent used in the electrochemichromic solution of the present invention -- i.e., being only soluble to the extent necessary to act upon the anodic compound -- so that it may be easily removed by conventional separation means, such as filtering, decanting or the like. When the redox agent is substantially insoluble in the solvent employed therewith, it may alternatively be advantageous to solubilize the redox agent and the anodic compound in water and, once the redox reaction has occurred, thereafter extract the anodic compound (now bearing an altered valence state) from the aqueous solution with a substantially water-immiscible electrochemichromic solvent. Alternatively, the redox agent may indeed be soluble in that solvent, provided that it may be readily removed by other conventional separation means -- e.g., centrifuging, precipitating, extracting, fractionating, osmosis, vacuum or other separation means known to one of ordinary skill in the art. Although it is generally preferable to use a molar excess of an insoluble redox agent, when a soluble redox agent is employed, it may be advantageous to use only about a stoichiometric amount thereof so that no excess redox agent is permitted to remain and thus interfere with subsequent reactions that the electrochemichromic compounds present in solution may undergo.

While the redox agent to be used in the context of the present invention will typically be a reducing agent, it is within the scope of the present invention for the redox agent to be an oxidizing agent as well. In this connection, an electrochemichromic compound may be contacted with an oxidizing agent to alter its valence state -- i.e., the compound assumes a higher valence state than its valence state prior to having been contacted with the oxidizing agent. For example, a viologen compound, such as $EVClO_4$, provided in its reduced colored form, may be employed. To a solution of this compound, an oxidizing agent, such as air or oxygen, may be introduced as a stream of bubbles to oxidize the reduced viologen compound to its substantially colorless form so that it serves as a cathodic compound. Excess oxidizing agent should thereafter be removed. Where a gaseous oxidizing agent is employed, the application of a vacuum -- i.e., a reduced atmospheric pressure -- or the introduction of a stream of bubbles of an inert gas should drive the excess gaseous oxidizing agent from the solution. In this instance, an anodic compound or combination of anodic compounds may then be added to the solution.

After removing that amount (if any) of redox agent that has remained unreacted, an anodic compound may

be introduced to this solution. The anodic compound, or combination of anodic compounds, chosen should bear a redox potential in the solvent that is greater than the redox potential of the cathodic compound in that solvent. Once combined in solution, these two electrochemichromic compounds now act in concert like redox indicators.

The anodic compound and the cathodic compound (both typically present in solution initially in their respective substantially colorless or least colored forms), should reach a total electrochemichromic compound concentration in solution of about 0.005 M to about 0.5 M, with a level of about 0.04 M being preferred. The ratio of total anodic compound to total cathodic compound may be in the range of about 5:1 to about 1:5, with a ratio of about 1:1 being preferred. In addition, as discussed supra, it is contemplated by the present invention that this range be inclusive of the fact that the anodic compound may be comprised of different individual anodic compounds and that the cathodic compound may be comprised of different individual cathodic compounds in these electrochemichromic solutions or, for that matter, different individual anodic compounds and different individual cathodic compounds may be employed simultaneously within an electrochemichromic solution of the instant invention.

It is further contemplated that, alternatively, the cathodic compound may be contacted with a redox agent to alter its valence state. This compound (now bearing an altered valence state) may then be introduced to a solution containing an anodic compound (or combination of anodic compounds wherein one of such anodic compounds does not require a redox pre-treatment to render it useful in this connection), wherein the anodic compound is in its ground valence state or a lower valence state than the valence state that it will reach at steady state equilibrium. For instance, when the cathodic compound is $EVClO_4$, it may be placed in solution and thereafter contacted with a redox agent -- e.g., a reducing agent -- to alter its valence state thereby producing a solution bearing intense color. A solution of an anodic compound, in this case, MVTB (X), PT (XI), MPT (XII), BMPT (XIII), POZ (XIV), APOZ (XV), AAPOZ (XVI), MPOZ (XVII), BPOZ (XVIII), HPOZ (XIX), KEPA (XX), AA (XXI), AB (XXII), AC (XXIII), MB (XXIV), TH (XXV), DCI(XXVI), or combinations thereof, or any of the foregoing in combination with an anodic compound that does not require a redox pre-treatment to render it useful in this connection, may then be added dropwise to the solution containing the reduced cathodic compound so as to act as a redox agent itself -- i.e., an oxidizing agent -- and oxidize the reduced cathodic compound (in what amounts to a titration) to form, at its stoichiometric end-point, a substantially colorless solution. In this way, the electrochemichromic compounds also act in concert similar in behavior to redox indicators. The resulting solution may then be used as the electrochemichromic solutions described above to manufacture devices capable of coloring when an applied potential is introduced thereto.

Since, after contacting, in the typical operation this invention, the anodic compound with a redox agent -- e.g., a reducing agent, such as zinc -- substantially none of that redox agent will remain in the solution (either in a soluble form or an insoluble form), the cathodic compound may become solubilized without itself becoming reduced (and subsequently changing color) while the anodic compound may remain in a reduced form, also substantially free of color. Thus, when no applied potential is introduced to this solution, the anodic compound is present in solution in a reduced, substantially colorless form and the cathodic compound is present in solution in an oxidized, substantially colorless form -- i.e., as it was when initially introduced into the solution.

The electrochemichromic solutions of the present invention, and the constituents thereof, may be flushed with anhydrous nitrogen, or any other anhydrous inert gas, prior to, and during, use and storage in order to minimize the concentration of oxygen and, if the solvent is non-aqueous, water present therein. Conventional techniques may be employed to reduce and limit the concentrations of those above-noted materials that are deemed undesirable for the instant invention. For example, anhydrous nitrogen gas may be bubbled through an electrochemichromic solution to decrease the oxygen concentration therein. Solvents or liquid electrochemichromic constituents may alternatively, or additionally, be contacted with activated alumina or the like, in the preparation of the electrochemichromic solution. Solid electrochemichromic compounds, and other solid constituents of this electrochemichromic solutions, may be dried prior to use by elevating the temperature of their immediate environment to about 110°C, or to a temperature not to exceed its melting or decomposition temperature, with an Abderhalden drying apparatus using a suitable anhydrous solvent, such as toluene [commercially available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin (1986)]. Other than any of these aforementioned measures that might be employed in an attempt to reduce and limit the concentrations of oxygen and water in the solutions of the present invention, these solutions may be prepared in accordance with conventionally known methods, typically at room temperature, by simply placing the appropriate amounts of electrochemichromic compounds, or other constituents described in the instant teaching, in a disclosed solvent to achieve the desired concentrations.

Reference to Figures 1 and 2 is now made in order to more faithfully describe the operation of the cell containing these electrochemichromic solutions. It is seen that the cell 1 includes two substantially planar glass substrates 2,3 positioned substantially parallel to one another. It is preferable that these glass substrates 2,3

be positioned as close to parallel to one another as possible so as to avoid double imaging, which is particularly noticeable in mirrors, especially when in a colored state.

Inasmuch as a source of an applied potential need be introduced to the cell 1 so that solution coloring in a rapid, intense and uniform manner may be observed, that source may be connected by electrical leads 9 to conducting strips known in the art as "bus bars". The bus bars 8 may be constructed of copper, aluminum or silver and should be affixed to conductive coatings 4 which are coated on each of the interior faces of these glass substrates 2,3. An exposed portion of the conductive coatings 4 may be provided for the bus bars 8 to adhere due to the spaced-apart relationstip and the displacement in opposite directions relative to one another -- i.e., laterally from, but parallel to the cavity which is created in the cell by the glass substrates 2,3 and the sealing means 5 -- of the coated glass substrates 2,3.

As stated above, a transparent conductive coating 4 is coated on each of the interior faces of these glass substrates 2,3. While the conductive coatings 4 should be of substantially uniform thickness, they may each have the same uniform thickness or different uniform thicknesses relative to each other. The conductive coatings 4 are generally from about 300 Å to about 10,000 Å in thickness having a refractive index in the range of about 1.6 to about 2.2. Preferably, conductive coatings 4 with a thickness of about 1,200 Å to about 2,300 Å having a refractive index of about 1.7 to about 1.9 are chosen depending on the desired appearance of the glass when the electrochemichromic solution contained therein is colored.

The conductive coatings 4 should also be highly and uniformly conductive in each direction to provide a substantially uniform response once an applied potential is introduced to the solution. And, the conductive coatings 4 should be inert to the constituents of the electrochemichromic solutions so that the constituents thereof do not anodically oxidize or cathodically reduce in preference to the electrochemichromic compounds present in the solution.

The sheet resistance of these transparent conductive glass substrates 2,3 may be between about 1 ohms per square to about 100 ohms per square, with about 6 ohms per square to about 20 ohms per square being preferred [ITO-coated glass substrates may be obtained commercially, for instance, from Donnelly Corporation, Holland, Michigan or, alternatively, tin oxide-coated glass substrates may be obtained commercially from Libbey-Owens-Ford Co., LOF Glass Division, Toledo, Ohio as "TEC-Glass" products, such as "TEC 10" (10 ohms per square sheet resistance), "TEC 12" (12 ohms per square sheet resistance) and "TEC 20" (20 ohms per square sheet resistance) tin oxide-coated glass].

The transparent conductive-coated substrates may be of the full-wave length-type ("FW") (about 6 ohms per square to about 8 ohms per square sheet resistance), the half-wave length-type ("HW") (about 12 ohms per square to about 15 ohms per square sheet resistance) or the half-wave length green-type ("HWG") (about 12 ohms per square to about 15 ohms per square sheet resistance). Bearing in mind that the thickness of these transparent conductive-coated substrates may vary as much as about 100 to about 200 Å, FW is about 3,000 Å in thickness, HW is about 1,500 Å in thickness and HWG is about 1,960 Å in thickness. HWG has a refractive index of about 1.7 to about 1.8, and has an optical thickness of about five-eighths to about two-thirds wave. HWG is generally chosen for electrochemichromic devices, especially reflective devices, such as mirrors, whose desired appearance has a greenish hue in color when an applied potential is introduced to the electrochemichromic solution.

The conductive coatings 4 may be constructed from the same material or different materials, including tin oxide, indium tin oxide ("ITO"), ITO full wave, ITO half wave, ITO half wave green, antimony-doped tin oxide, fluorine-doped tin oxide, antimony-doped zinc oxide, aluminum-doped zinc oxide, with ITO being preferred. However, where the ultraviolet stability of the device is a concern, tin oxides or zinc oxides are preferred.

As stated above, the spaced-apart transparent conductive-coated glass substrates 2,3, have sealing means 5 positioned therebetween to define the cell cavity. The sealing means 5 may be constructed of any material inert to the constituents of the electrochemichromic solutions and any subsequently formed by-products thereof. To that end, the sealing means may be chosen from the following materials including, but not limited to, various thermosetting materials, such as epoxy resins and silicones, various thermoplastic materials, such as plasticized polyvinyl butyral, polyvinyl chloride, paraffin waxes, ionomer resins, various inorganic materials and the like. For a further recitation of suitable sealing materials, see United States Patent 4,761,061 (Nishiyama).

The thickness of the sealing means 5 may vary from about 10 μm to about 1,000 μm. Preferably, however, this thickness is about 50 μm to about 125 μm. The thickness of the sealing means 5 determines the thickness of the interpane space created between the glass substrates 2,3 by the sealing means 5 -- i.e., the cell gap. Thus, it is the sealing means 5 which spaces or separates the transparent conductive-coated glass substrates 2,3 from one another. In addition, sealing means 5 may prevent escape of the electrochemichromic solution 6 from the cell cavity or, for that matter, penetration of environmental contaminants into the cell cavity.

In order to fill the cell 1, a small gap -- e.g., about 2 mm x 1 mm x 150 μm -- may be allowed to remain in

the sealing means 5 so that an electrochemichromic solution 6 may be placed into the cell cavity during a conventional vacuum backfilling process. In the vacuum backfilling process, the empty electrochemichromic device may be placed in a chamber having reduced atmospheric pressure therein -- i.e., about 1 mm Hg or lower. A container -- e.g., a dish or small cup -- of the solution 6 should also be placed in this chamber so that it may fill the cell cavity through the fill hole. The fill hole of the device may then be lowered just beneath the surface of the solution in the container. When the chamber is vented to atmospheric pressure, the solution 6 is thereby forced into the cell cavity and consequently fills it.

Alternatively, the cell cavity may be formed by positioning a thermoplastic sheet, constructed of an ionomer resin, a plasticized polyvinyl butyral or the like, onto the interior surface of one of the transparent conductive-coated glass substrates 2. This sheet may be trimmed to size about the outer periphery of one of the transparent conductive-coated glass substrates 2 after it is placed thereover. The interior portion of the thermoplastic sheet may thereafter be trimmed so that only a border of this sheet remains about the periphery of the transparent conductive-coated glass substrate 2. Before curing the thermoplastic sheet so that it forms the sealing means 5, an electrochemichromic solution 6 according to the present invention may be dispensed onto the surface of one of the transparent conductive-coated glass substrates 2. It is of no moment that a portion of the solution may escape under or over the sheet, because the other transparent conductive-coated glass substrate 3 is thereafter placed in contact therewith so that the thermoplastic sheet is positioned between the transparent conductive-coated glass substrates 2,3 and the cell cavity which is created as a result becomes filled with the solution 6.

This construction is then temporarily clamped together and thereafter baked in an oven at a temperature of about 25°C to about 120°C to cure the thermoplastic sheet into the sealing means 5 that will keep intact the integrity of the cell housed in the device.

Once assembled and filled, an applied potential may be introduced to the device by the bus bars 8 in order to induce solution coloring. The applied potential may be supplied from a variety of sources including, but not limited to, any source of alternating current ("AC") or direct current ("DC") known in the art, provided that, if an AC source is chosen, control elements, such as diodes, should be placed between the source and the conductive coatings 4 to ensure that the potential difference between the conductive coatings 4 does not change polarity with variations in polarity of the applied potential from the source. Suitable DC sources are storage batteries, solar thermal cells, photovoltaic cells or photoelectrochemical cells.

The applied potential generated from any of these sources may be introduced to the solution in the range of about 0.001 volts to about 5.0 volts. Typically, however, an applied potential of about 0.2 volts to about 2.0 volts is preferred, with about 1 volt to about 1.5 volts particularly preferred, to permit the current to flow across the solution 6 thereby oxidizing and reducing the electrochemichromic compounds to cause solution coloring -- i.e., to change the amount of light transmitted therethrough.

A means for controlling the current created by the applied potential and delivered to the conductive coatings 4 is suggested so that the current, which thereafter disperses the potential uniformly throughout the solution 6, does not exceed the potential difference at which irreversible reactions occur -- e.g., solvent electrolysis, redox reactions involving the inert electrolytic material, or reactions which degrade the electrochemichromic compound. The means for controlling the current delivered to the conductive coatings 4 may be manually or automatically operated.

The solutions of the present invention, once prepared, may be advantageously employed to manufacture devices using electrochemichromic cells, such as, mirrors -- e.g., vehicular, architectural or specialty mirrors, such as those useful in periscopic or dental applications --, windows -- e.g., architectural or automotive glazings like sun roofs, sun visors or shade bands --, information displays, optically attenuating contrast filters, privacy or security partitions, lenses and the like.

In the context of a mirror assembly, a reflective coating 7, having a thickness in the range of 250 Å to about 2,000 Å, preferably about 1,000 Å, should thereafter be applied to the exterior face of one of the transparent conductive-coated glass substrates 3 in order to form a mirror. Suitable materials for this layer are aluminum, palladium, platinum, titanium, chromium, silver and stainless steel, with silver being preferred. As an alternative to such metal thin film reflectors, multi-coated thin film stacks of dielectric materials or a high index single dielectric thin film coating may be used as a reflector. The reflective coating 7 serves not only to assist in reflecting incident light but also in conducting an applied potential to the conductive coatings 4.

It is clear from the teaching herein that should a window, sun roof or the like be desirably constructed, the reflective coating 7 need only be omitted from the assembly so that the light which is transmitted through the transparent panel is not further assisted in reflecting back therethrough.

It is also clear, that only one of the substrates that comprise the device need be at least substantially transparent. That is, provided that a surface of a conductive coating 4 of the other substrate is in contact with the electrochemichromic solution 6, a functioning device in accordance with the teaching herein may be furnished.

Specifically, in a mirror device, a polished metal plate or a metal-coated glass substrate may be used or, in a display device, a conductive ceramic material may be suitably employed inasmuch as these materials are physically, chemically and electrochemically compatible with the electrochemichromic solutions themselves.

Having stated the relationship between a mirror assembly and a window assembly in connection with the teaching of the present invention, it should also be readily understood by the art-skilled that the term "transmittance" refers to the amount of light that may pass through -- i.e., transmitted through -- an electrochemichromic solution that is contained, for example, within an electrochemichromic window assembly. On the other hand, the term "reflectance" refers to the amount of light that may pass through -- i.e., transmitted through -- an electrochemichromic solution and thereafter reflect off a reflective coating placed on the back of one of the glass substrates of, for example, an electrochemichromic mirror assembly and thereafter pass back through the solution in substantially the same direction from which it originated.

In addition, one of the transparent conductive-coated glass substrates 2 should preferably be of a laminate assembly comprising at least two transparent panels affixed to one another by a substantially transparent adhesive material. This laminate assembly assists in reducing the scattering of glass shards from the glass substrate 2 should the mirror assembly break due to impact. While the term "glass" has been employed throughout the instant disclosure, it is intended by the teaching herein that that term also include optical plastics, such as polycarbonate, acrylic and polystyrene, as well as tempered glass and laminated glass.

Once constructed, the electrochemichromic device -- e.g., a mirror or window assembly -- may have a molded casing placed therearound. This molded casing may be pre-formed and then placed about the periphery of the assembly or, for that matter, injection molded therearound using conventional techniques, including injection molding of thermoplastic materials, such as polyvinyl chloride or propylene, or reaction injection molding of thermosetting materials, such as polyurethane or other thermosets. These techniques are well-known in the art [see, e.g. United States Patents 4,139,234 (Morgan) and 4,561,625 (Weaver), respectively, for a discussion of those techniques in the context of modular window encapsulation].

Each of the documents cited in the present teaching is herein incorporated by reference to the same extent as if each document had individually been incorporated by reference.

The superior rapidity, intensity and uniformity of solution coloring and the redox pre-treatment of at least one of the electrochemichromic compounds distinguishes the present teaching from the electrochemichromic solutions known heretofore and sets the present invention separate and apart therefrom.

In view of the above description of the instant invention, it is evident that a wide range of practical opportunities is provided by the teaching herein. While the following examples (except for Example 13, infra) illustrate the benefits and utility of the present invention with respect to mirrors, it is clear based on the disclosure provided herein that comparable benefits and utility may be, and have been, achieved with glazings, such as windows and sun roofs; partitions; information displays; optically attenuating contrast filters; lenses and the like. And, these examples of electrochemichromic assemblies are provided to illustrate the utility of the present invention only and are not to be construed so as to limit in any way the teaching herein.

EXAMPLES

The constituents identified in the present invention may be obtained commercially from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin or many other chemical suppliers, unless otherwise indicated. In fact, several anodic compounds of the present invention, such as IV, VI and XXVI, are commercially available in their ionic form, and were used as such.

MVTB Examples

Example 1

To demonstrate the difference between an electrochemichromic solution of the present invention from those electrochemichromic solutions of the prior art with respect to uniform coloring and the concomitant Iris effect, we formulated two solutions and used them in interior rearview automotive mirrors constructed as depicted in Figures 1 and 2. These silvered mirrors each have a cell gap of about 80 μm with ITO-coated glass substrates having about 8 ohms per square sheet resistance and the following approximate dimensions: 6 cm x 25 cm x 2 mm.

In the first mirror, we placed an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of DMPA (as the anodic compound), both dissolved in the solvent propylene carbonate.

In the second mirror, we placed an electrochemichromic solution prepared according to the present in-

vention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced MVTB (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the MVTB reduction, we first placed about 0.5 grams (0.002 moles) of MVTB into about 100 mls of a solvent comprising the combination of about 99% propylene carbonate and about 1% acetic acid (v/v) under substantially inert conditions at about ambient temperature to about 50°C to form a blue colored solution. We then added, with stirring, about 2 grams of zinc dust (325 mesh) thereto for a period of about 15 minutes to about 45 minutes after which period of time the solution became substantially colorless by reaching a pale yellow color. We performed this reaction under substantially the same conditions as those recited above. We removed that quantity of zinc dust which remained unreacted by filtration and thereafter contacted the substantially colorless MVTB solution (now in a reduced valence state) with the $EVClO_4$ to reach a pale bluish green solution color.

We introduced an applied potential of about 1.0 volt to each of the filled mirrors, and thereafter observed that the second mirror, filled with an electrochemichromic solution of the present invention, colored rapidly and uniformly with a negligible Iris effect as compared with the first mirror, filled with an electrochemichromic solution of the prior art.

In addition, we observed that the high reflectance at the center portion of the second mirror decreased from about 66% to about 13% in a response time of about 1.5 seconds when a potential of about 1.0 volt was applied thereto as compared with a decrease to only about 37% in the first mirror as determined by a reflectometer -- set in reflectance mode -- equipped with a light source (known in the art as Illuminant A) and a photopic detector attached to a strip chart recorder. What's more, we observed that the second mirror bleached from about 16% reflectance to about 60% reflectance in a response time of about 1.2 seconds under about zero applied potential. Since the first mirror colored to only about 37%, a fair comparison with the second mirror could not be made.

Example 2

We used the electrochemichromic solutions described in Example 1, supra, to fill two interior rearview automotive mirrors each having about a 100 μm cell gap and constructed from ITO-coated glass substrates having about 12 ohms per square sheet resistance. Upon application of about 1.0 volt, we observed that the second mirror, filled with an electrochemichromic solution of the present invention, colored uniformly and rapidly whereas the first mirror, filled with an electrochemichromic solution of the prior art, did not color uniformly and the electrochemichromic response obtained was less rapid. And, the second mirror demonstrated an intense bluish purple color as compared with the largely dark green color with a slight purple tint demonstrated by the first mirror.

Specifically, we observed the second mirror to exhibit color formation of about 70% reflectance to about 20% reflectance in a response time of about 1.3 seconds when a potential of about 1.0 volt was applied thereto as compared with the first mirror which registered substantially the same reflectance effect in about 4.3 seconds. We also observed that the second mirror and the first mirror demonstrated a comparable rate of bleaching -- about 1.8 seconds under about zero applied potential as compared with about 1.6 seconds, respectively -- from about 20% reflectance to about 60% reflectance. In addition, we noted that although the two mirrors exhibited no marked difference with respect to their high reflectance percentage in the bleached state -- about 72.6% for the second mirror and about 74.4% for the first mirror --, the second mirror showed an improvement over the first mirror with respect to decreased reflectance -- i.e., about 7.9% as compared with about 16.0%, respectively. We made and recorded these observations by the detection method described in Example 1, supra.

Example 3

We also used the electrochemichromic solutions described in Example 1, supra, to fill two automotive mirrors each having about a 135 μm cell gap and constructed from ITO-coated glass substrates having about 12 ohms per square sheet resistance to illustrate the more intense color formation demonstrated by the electrochemichromic solutions of the present invention. We constructed a cell having a wider cell gap than in the previous examples to illustrate the enhanced uniform coloring of the solutions of the instant invention when Iris effects are lessened or eliminated. When we introduced an applied potential of about 1.0 volt to each mirror, we observed that the second mirror yielded a low reflectance of about 6.9% whereas the first mirror yielded a reflectance of only about 10.8%. We made and recorded these observations using the detection method described in Example 1, supra.

Example 4

We next used the electrochemichromic solutions as described in Example 1, supra, to demonstrate the ability of the electrochemichromic solutions of the present invention to be employed with high resistive glass -- an inferior quality and accordingly less expensive glass -- and afford similarly superior results over those electrochemichromic solutions of the prior art. To this end, we filled two mirrors each having about a 350 μm cell gap and constructed from ITO-coated glass substrates having about 80 ohms per square sheet resistance. Upon introducing an applied potential of about 1.0 volt to each of the mirrors, we observed that the second mirror yielded a low reflectance of about 5.7% whereas the first mirror yielded a reflectance of only about 34% and also exhibited an Iris effect even with the larger cell gap. We made and recorded these observations using the detection method described in Example 1, supra.

Example 5

In this example, we used another preferred solvent, the combination of about 79% 3-ethoxypropionitrile, about 20% 2-acetylbutyrolactone and about 1% glacial acetic acid (v/v), to further demonstrate the enhanced characteristics with respect to uniform coloring and the concomitant Iris effect of the solutions of the present invention over those of the prior art.

In that regard, we constructed two interior rearview automotive mirrors each having a cell gap of about 50 μm with ITO-coated glass substrates having about 6 to about 8 ohms per square sheet resistance.

In the first mirror, we placed an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ and about 0.02 M of DMPA, both dissolved in a solvent comprising about 80% 3-ethoxypropionitrile and about 20% 2-acetylbutyrolactone (v/v). In addition, this solution contained about 5% of "UVINUL 400" (w/v) as an ultraviolet stabilizing agent.

In the second mirror, we placed an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ and about 0.02 M of reduced MVTB, both dissolved in a solvent comprising about 79% 3-ethoxypropionitrile, about 20% 2-acetylbutyrolactone and about 1% glacial acetic (v/v). In addition, this solution contained about 5% of "UVINUL 400" (w/v) as an ultraviolet stabilizing agent. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

After we prepared each mirror with the electrochemichromic solutions as described above, we introduced an applied potential of about 1.0 volt to each of the mirrors. The second mirror demonstrated an intense purple color as compared with the light green color demonstrated by the first mirror. In addition, in the bleached state, the second mirror displayed a clear yet silvery appearance while the first mirror displayed an almost clear appearance with a slightly yellow hue. Moreover, the second mirror demonstrated a fairly uniform coloring and a very small Iris effect in contrast to the non-uniform coloring and large Iris effect displayed by the first mirror.

We observed that the high reflectance was about 75.3% as compared with 79.2% for the first mirror. And, the reflectance at the center portion of the second mirror decreased from about 70% to about 20% in a response time of about 1.0 second when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 13.1% as compared with the first mirror which decreased from about 70% to only about 37% in about the same period of time, with an ultimate decrease to about 23.8% after about 2.9 seconds.

With respect to bleaching, we observed that the second mirror and the first mirror demonstrated comparable response times in connection with their ability to bleach. That is, in the range from about 20% reflectance to about 70% reflectance, the second mirror bleached in about 0.9 seconds under about zero applied potential whereas the first mirror achieved the same results in about 1.0 second. We made and recorded these observations using the detection method described in Example 1, supra.

Example 6

In the example, we used a combination of about 69% 3-ethoxypropionitrile, about 30% propylene carbonate and about 1% glacial acetic acid (v/v) as a solvent as yet another demonstration of the enhanced characteristics with respect to uniform coloring and the concomitant Iris effect of the solutions of the present invention over those of the prior art.

We constructed two interior rearview automotive mirrors as in Example 5, supra. In the first mirror, we placed an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ and about 0.02 M of DMPA, both dissolved in a solvent comprising about 70% 3-ethoxypropionitrile and about 30% propylene carbonate.

In the second mirror, we placed an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ and about 0.02 M of reduced MVTB dissolved in a solvent com-

prising about 69% 3-ethoxypropionitrile, about 30% propylene carbonate and about 1% glacial acetic (v/v). As in Example 1, supra, Prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

After we prepared each mirror with the electrochemichromic solutions as described above, we introduced an applied potential of about 1.0 volt to each of the mirrors. The second mirror demonstrated intense purple color as compared with the light green color demonstrated by the first mirror. In addition, in the bleached state, the second mirror displayed a clear yet silvery appearance while the first mirror displayed an almost clear appearance with a slight yellow hue. Moreover, the second mirror demonstrated a fairly uniform coloring and a very small Iris effect in contrast to the non-uniform coloring and large Iris effect displayed by the first mirror.

We further observed that the high reflectance at the center portion of the second mirror was about 76.5% as compared with about 78.7% for the first mirror. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.0 second when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 13.1% as compared with the first mirror which decreased from about 70% to only about 41% in about the same period of time, with an ultimate decrease to about 24.3% after about 2.2 seconds. We also observed that the second mirror and the first mirror demonstrated comparable response times in connection with their ability to bleach. We made and recorded these observations using the detection method described in Example 1, supra.

Example 7

In order to demonstrate the enhanced intensity of the color formed by the electrochemichromic solutions of the present invention which thereby effectively decreases the reflectance percentage, we constructed two interior rearview automotive mirrors each having a cell gap of about 135 μm with ITO-coated glass substrates having about 12 ohms per square to about 15 ohms per square sheet resistance.

In the first mirror, we placed an electrochemichromic solution comprising about 0.01 M of $EVClO_4$ and about 0.01 M solution of DMPA, both dissolved in a solvent comprising about 80% 3-ethoxypropionitrile and about 20% 2-acetylbutyrolactone (v/v). In addition, this solution contained about 5% of "UVINUL 400" (w/v) as an ultraviolet stabilizing agent.

In the second mirror, we placed an electrochemichromic solution prepared according to the present invention comprising about 0.01 M of $EVClO_4$ and about 0.01 M solution of reduced MVTB, both dissolved in a solvent comprising about 80% 3-ethoxypropionitrile and about 20% 2-acetylbutyrolactone (v/v). In addition, this solution contained about 5% of "UVINUL 400" (w/v) as an ultraviolet stabilizing agent. We dissolved the MVTB in a solvent comprising about 80% 3-ethoxypropionitrile and about 20% 2-acetylbutyrolactone (v/v), then reacted the solubilized MVTB with zinc dust and otherwise followed the protocol indicated in Example 1, supra.

After we prepared each mirror with the electrochemichromic solutions as described above, we introduced an applied potential of about 1.0 volt to each of the mirrors. The second mirror demonstrated an intense bluish purple color as compared with the light to dark green color demonstrated by the first mirror. In addition, in the bleached state, the second mirror displayed a clear yet silvery appearance while the first mirror displayed an almost clear, yet slightly yellow, non-silvery, appearance. Moreover, the second mirror demonstrated uniform coloring and no appreciable Iris effect in contrast to the non-uniform coloring with a lighter green color which formed in the center of the mirror and a small Iris effect displayed by the first mirror.

We further observed that the high reflectance at the center portion of the second mirror was about 73.5% as compared with about 80.2% for the first mirror. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.4 seconds when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 10.2%, as compared with the first mirror which decreased from about 70% to only about 40% in about the same period of time, with an ultimate decrease to about 20.2%. We made and recorded these observations using the detection method described in Example 1, supra.

Example 8

In Examples 8 and 9, we used combinations of 3-hydroxypropionitrile and glutaronitrile as the solvent to still further demonstrate the benefits of the solutions of the present invention.

We constructed two interior rearview automotive mirrors each having a cell gap of about 100 μm with ITO-coated glass substrates having about 12 ohms per square to about 15 ohms per square sheet resistance.

In the first mirror, we placed an electrochemichromic solution comprising about 0.035 M of $EVClO_4$ and about 0.035 M of DMPA, both dissolved in a solvent comprising about 75% 3-hydroxypropionitrile combined with about 25% glutaronitrile (v/v). In addition, we placed about 5% of "UVINUL 400" (w/v) in this solution.

In the second mirror, we placed an electrochemichromic solution comprising about 0.0175 M of $EVClO_4$

and about 0.0175 M of reduced MVTB, both dissolved in a solvent comprising about 74% 3-hydroxypropionitrile, about 25% glutaronitrile and about 1% glacial acetic acid (v/v). In addition, we placed about 5% of "UVINUL 400" (w/v) in this solution. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

We then introduced an applied potential of about 1.0 volt to each of the mirrors, and thereafter observed that the second mirror, filled with an electrochemichromic solution of the present invention, colored rapidly with excellent uniformity and without an appreciable Iris effect as compared with the first mirror. We observed an intense bluish purple color as compared with the largely dark green color demonstrated by the first mirror.

In addition, we observed that the high reflectance at the center portion of the second mirror was about 79.5% as compared with 74.7% in the first mirror. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.7 seconds when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 8.6%, while the first mirror decreased from about 70% to only about 37% in about the same period of time, with an ultimate decrease to about 13.7% after about 5.3 seconds. We also observed that the second mirror bleached from about 20% reflectance to about 60% reflectance in a response time of about 1.9 seconds under about zero applied potential as compared with the first mirror which bleached to about the same degree in about 2.2 seconds. When in the bleached state, the second mirror displayed a clear and silvery appearance while the first mirror displayed a clear appearance with a slight yellow hue.

The numerical values obtained in connection with these observations were made using the detection method described in Example 1, supra.

Example 9

In this example, we used a combination of about 49.5% 3-hydroxypropionitrile, about 49.5% glutaronitrile and about 1% glacial acetic acid (v/v) to construct an interior rearview automotive mirror having a cell gap of about 100 μm with ITO-coated glass substrates having about 12 ohms per square to about 15 ohms per square sheet resistance.

We constructed this mirror with an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ and about 0.02 M of reduced MVTB, both dissolved in a solvent comprising about 49.5% 3-hydroxypropionitrile, about 49.5% glutaronitrile and about 1% glacial acetic acid (v/v) placed between the substrates. In addition, we placed about 5% of "UVINUL 400" (w/v) to this solution. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

We then introduced an applied potential of about 1.0 volt to the mirror, and thereafter observed that the mirror colored rapidly with excellent uniformity and without an appreciable Iris effect. We thereafter observed the formation of an intense bluish purple color.

In addition, we observed that the high reflectance at the center portion of the mirror was about 74.3%. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.5 seconds when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 7.7%. We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.7 seconds under about zero applied potential. When in the bleached state, the mirror displayed a clear appearance.

The numerical values obtained in connection with these observations were made using the detection method described in Example 1, supra.

Example 10

In this example, we used the combination of about 69% 3-hydroxypropionitrile, about 30% 3,3′-oxydipropionitrile and about 1% glacial acetic acid (v/v) as a solvent in connection with the construction of an electrochemichromic interior rearview automotive mirror. This mirror was constructed from ITO-coated glass substrates having a cell gap of about 100 μm with about 12 ohms per square to about 15 ohms per square sheet resistance.

We placed an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ and about 0.02 M of reduced MVTB, both dissolved in a solvent comprising about 69% 3-hydroxypropionitrile, about 30% 3,3′-oxydipropionitrile and about 1% glacial acetic acid (v/v). In addition, we placed about 5% of "UVINUL 400" (w/v) to this solution. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

We then introduced an applied potential of about 1.0 volt to the mirror, and thereafter observed that the mirror colored rapidly with excellent uniformity and without an appreciable Iris effect. We thereafter observed the formation of an intense bluish purple color.

In addition, we observed that the high reflectance at the center portion of the mirror was about 73.2%. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.5 seconds when a potential of about 1.0 volt was applied thereto, with an ultimate decrease to about 6.9%. What's more, we observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.7 seconds under about a zero applied potential. When in the bleached state, the mirror displayed a clear and silvery appearance.

The numerical values obtained in connection with these observations were made using the detection method described in Example 1, supra.

Example 11

In this example, we used the combination of about 69% 3-ethoxypropionitrile, about 30% 3-hydroxypropionitrile and about 1% glacial acetic acid (v/v) as a solvent in connection with the construction of an electrochemichromic interior rearview automotive mirror. This mirror was constructed from ITO-coated glass substrates having a cell gap of about 100 μm with about 12 ohms per square to about 15 ohms per square sheet resistance.

We placed an electrochemichromic solution comprising about 0.02 M of $EVClO_4$ and about 0.02 M of reduced MVTB, both dissolved in a solvent comprising about 69% ethoxypropionitrile, about 30% 3-hydroxypropionitrile and about 1% glacial acetic acid (v/v). In addition, we placed about 5% of "UVINUL 400" (w/v) to this solution. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

We then introduced an applied potential of about 1.0 volt to the mirror, and thereafter observed that the mirror colored rapidly with excellent uniformity and without an appreciable Iris effect. We thereafter observed the formation an intense bluish purple color.

In addition, we observed that the high reflectance at the center portion of the mirror was about 72.4%. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.7 seconds, with an ultimate decrease to about 9.4%. Moreover, we observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.2 seconds. When in the bleached state, the mirror displayed a clear appearance.

The numerical values obtained in connection with these observations were made using the detection method described in Example 1, supra.

Example 12

In this example, we used the combination of about 99% propylene carbonate and about 1% glacial acetic acid (v/v) as a solvent in connection with the construction of an electrochemichromic interior rearview automotive mirror. This mirror was constructed from ITO-coated glass substrates having a cell gap of about 50 μm with about 6 to about 8 ohms per square sheet resistance.

We placed an electrochemichromic solution comprising about 0.025 M of $EVClO_4$ and about 0.025 M of reduced MVTB, both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v). In addition, we placed about 5% of "UVINUL 400" (w/v) to this solution. As in Example 1, supra, prior to combining the anodic and cathodic compounds, we reacted MVTB with zinc and otherwise followed the protocol indicated.

We then introduced an applied potential of about 1.0 volt to the mirror, and thereafter observed that the mirror colored rapidly with excellent uniformity and without an appreciable Iris effect. We thereafter observed the formation of an intense bluish purple color.

In addition, we observed that the high reflectance at the center portion of the mirror was about 76.3%. And, the reflectance decreased from about 70% to about 20% in a response time of about 1.1 seconds, with an ultimate decrease to about 14.5%. What's more, we observed that the mirror bleached from low reflectance to about 60% reflectance in a response time of about 0.7 seconds. When in the bleached state, the mirror displayed a clear and silvery appearance.

The numerical values obtained in connection with these observations were made using the detection method described in Example 1, supra.

Example 13

A window assembly or a sun roof assembly may also be constructed using the electrochemichromic solutions of the present invention. To that end, we constructed a sun roof assembly employing the subject solu-

tions.

We constructed an automotive sun roof from tin oxidecoated glass having about 10 ohms per square sheet resistance [commercially available as "TEC-Glass" products from Libbey-Owens-Ford Co., LOF Glass Division, Toledo, Ohio]. The dimensions of the sun roof were approximately 38 cm x 60 cm, with a cell gap of about 380 μm between the two tin oxide-coated glass substrates. The integrity of this cell gap was kept intact by a sealing means constructed of plasticized polyvinyl butyral which also ensured that the electrochemichromic solution remained therein.

We prepared an electrochemichromic solution according to the present invention whose constituents included about 0.01 M of MVTB, that was previously reacted with zinc as in Example 1, supra, about 0.015 M of $EVClO_4$, about 0.05 M of tetraethylammonium perchlorate and about 5% of "UVINUL 400" (w/v). We prepared solutions of these constituents with a solvent comprising about 64% propylene carbonate, about 35% cyanoethyl sucrose and about 1% acetic acid (v/v).

After filling the cell in the sun roof with this solution, we introduced an applied potential of about 1.0 volt thereto and observed over a time period of about 2 minutes a change from about 74.5% to about 17% in the amount of light transmitted through the sun roof. When we applied zero potential, the electrochemichromic solution self-erased such that the amount of light transmitted therethrough was first observed at about 5% and then over a period of about 2 minutes the color lessened to the point that about 25% of the light was being transmitted through the solution. After a period of about 7 minutes, this solution completely self-erased. We made and recorded these observations using the detection method described in Example 1, supra, except that the reflectometer was set in transmission mode.

Example 14

In Example 14, we prepared four mirrors -- specifically, (A) and (B) two Class 8 truck mirrors, each having active dimensions of about 5.25" x 16.5", (C) a mirror having active dimensions of about 4.25" x 7.25" used on the sport utility vehicle manufactured and marketed by Ford Motor Co., Detroit, Michigan under the tradename "EXPLORER" and (D) an interior passenger mirror having active dimensions of about 2.5" x 10" -- containing an electrochemichromic solution comprising about 0.035 M reduced MVTB and about 0.035 M $EVClO_4$ dissolved in a combination of about 97% propylene carbonate and about 3% glacial acetic acid (v/v). To this solution, we also added about 12% of "UVINUL 400" (w/v).

To the first truck mirror [Example 14(A)], assembled from FW ITO-coated glass substrates having sheet resistance of about 6 ohms per square to about 8 ohms per square with a cell gap of about 100 μm, we applied a potential of about 1.3 volts. We observed this truck mirror to color rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 70.5% reflectance which decreased to a low reflectance of about 9.0% when a potential of about 1.3 volts was applied thereto. The response time for the reflectance to change from about 70% to about 20% when that potential was applied thereto was about 6.0 seconds. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 9.0 seconds under about zero applied potential.

To the second truck mirror [Example 14(B)], assembled from "TEC-Glass" (suppled by Libby-Owens-Ford Co., Toledo, Ohio) with the front clear glass having sheet resistance of about 20 ohms per square and the back silvered glass having sheet resistance of about 12 ohms per square with a cell gap of about 125 μm, we applied a potential of about 1.4 volts. We observed this truck mirror to color rapidly and uniformly, with a negligible Iris, to a bluish purple color with a greenish hue.

In addition, we observed that the high reflectance at the center portion of the second mirror was about 70.5% reflectance which decreased to a low reflectance of about 9.0% when about 1.4 volts was applied thereto. The response time for the reflectance to change from about 70% is about 20% when that potential was applied thereto was about 7.8 seconds. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 13.1 seconds under about zero applied potential.

To the "EXPLORER" mirror [Example 14(C)], assembled from HW ITO-coated glass substrates having about 12 ohms per square sheet resistance with a cell gap of 125 μm, we applied a potential of about 1.15 volts. We observed this mirror to color rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 7.6% reflectance which decreased to a low reflectance of about 8.9% when about 1.15 volts was applied thereto. The

response time for the reflectance to change from about 70% is about 20% when that potential was applied thereto was about 3.8 seconds. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 6.3 seconds under about zero applied potential.

To demonstrate thermal stability and cycle stability, we typically cycle the mirrors -- i.e., alternatively apply and remove a potential that triggers a change in reflectance -- at temperatures of about room temperature, about 50°C and about 85°C for a period of about 5,000 cycles to about 30,000 cycles. We typically run these color-bleach cycles at time intervals of about 3-5, 15-15, 30-30 and 30-60 seconds.

In this connection, we again observed the "EXPLORER" mirror after about 30,000 30-60 second color-bleach cycles under an applied potention of about 1.15 volts to color and about zero volts to bleach. We made and recorded these oberservations at a temperature of about 50°C and have illustrated them in Table 1 below.

Table 1

Example No.	High Reflectance %	Low Reflectance %	Color 70-20% R (Sec)	Bleach 10-60% R (sec)
14(C)	76.5	8.6	4.1	6.7

To the interior passenger mirror [Example 14(D)], assembled from "TEC-Glass" (supplied by Libbey-Owens-Ford Co., Toledo, Ohio) having sheet resistance of about 20 ohms per square with a cell gap of about 105 μm, we applied a potential of about 1.15 volts. We observed this mirror to color rapidly and uniformly, with a negligible Iris, to a bluish purple color with a greenish hue.

In addition, we observed that the high reflectance at the center portion of the mirror was about 65.4% reflectance which decreased to a low reflectance of about 6.8% when about 1.15 volts was applied thereto. The response time for the reflectance to change from about 65% to about 20% when that potential was applied thereto was about 2.4 seconds. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 5.9 seconds under about zero applied potential.

This mirror demonstrated very good cycle stability at about room temperature, about 50°C and about 85°C. Also, the mirror demonstrated excellent ultraviolet stability and thermal stability.

In general, we observed good ultraviolet stability, heat stability and cycle stability of the solutions of the present invention when contained within the devices described herein. Specifically, when MVTB is employed in conjunction with $EVClO_4$ in any of the solvents herein recited, a solution of even more ultraviolet stability is observed when compared with the combination of DMPA and $EVClO_4$ in that same solvent. Examples reflecting the demonstration of ultraviolet stability, thermal stability and cycle stability by the electrochemichromic solution of the present invention are illustrated in the MPT Examples, infra. We also observed greater rapidity of response times, especially when bleaching, with solutions having 3-ethoxypropionitrile as a solvent component.

The mirrors described in the following examples also demonstrate similar beneficial properties and utility to those mirrors containing solutions comprising reduced MVTB (described in Examples 1 through 14, supra). Some of those properties, and the attendant utility, are highlighted below in the following Examples.

MPT Examples

Although some of the electrochemichromic compounds described in the present application are commercially available, many are not. Thus, we have described at Example 15(A), infra, a synthesis of one of those compounds -- i.e., MPT. It is to be understood that although we have chosen to specifically illustrate the synthesis of this 2-methyl-phenothiazone derivative, this synthetic scheme is equally well-suited to produce other substituted phenothiazone derivatives as described in this application.

Example 15

A. Synthesis of MPT

In Example 15, we synthesized 2-methyl-phenothiazin-3-one according to the procedure described in Eu-

ropean Patent Application EP 0 115 394 (Merck Frosst Canada). That is, we stirred at about room temperature a solution of about 19.5 grams of methyl-1,4-benzoquinone in about 200 mls of methanol and added slowly thereto a solution of about 10 grams of o-aminothiophenol in about 15 mls of methanol over a period of time of about 1 hour. Once this addition was complete, we allowed the mixture to continue to stir at about room temperature for a period of time of about 2 hours. We then filtered off the red precipitate which formed, and thereafter washed this product twice with about 300 ml portions of methanol to obtain a greater than about 60% yield. We measured the melting point of the product to be about 186°C to about 188°C. Elemental analysis provided the following results: Theoretical: C, 68.72; H, 3.96; N, 6.17 and S, 14.10. Found: C, 68.98; H, 3.95; N, 6.25 and S, 14.61.

B. Use of MPT in Mirrors

We placed into a mirror, assembled according to Example 1 (except that we used a cell gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.025 M of $EVClO_4$ (as the cathodic compound) and about 0.025 M of reduced MPT (as the anodic compound), both dissolved in a solvent comprising about 98% propylene carbonate and about 2% glacial acetic acid (v/v).

In connection with the MPT reduction, we followed the reduction procedure as described in Example 20(A), infra.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.9% reflectance which decreased to a low reflectance of about 6.0% when about 1.3 volts was applied thereto. The response time for the reflectance to change from about 70% to about 20% when a potential of about 1.3 volts was applied thereto was about 1.7 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.0 seconds under about zero applied potential.

In this instance as a demonstration of thermal stability and cycle stability, we applied and removed a potential of about 1.3 volts at about 85°C to color and bleach, respectively, this electrochemichromic cell for about 100,000 3-5 second color-bleach cycles. After this period of cycling, we observed that the high reflectance at the center portion of the mirror was about 78.1% and the mirror colored to about 5.8% when a potential of about 1.3 volts was applied thereto. Reflectance changed from about 70% to about 20% in a response time of about 1.7 seconds when a potential of about 1.3 volts was applied thereto.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.7 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance was silvery indicating excellent thermal stability and cycle stability.

Examples 16 through 19

We repeated Example 15 using substantially equimolar solutions of reduced MPT and $EVClO_4$ in the following molar concentrations:

Example 16 -- about 0.04 M in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v);

Example 17 -- about 0.02 M in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v);

Example 18 -- about 0.04 M in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid, with about 5% of "UVINUL 400" (w/v) having been added as an ultraviolet stabilizing agent; and

Example 19 -- about 0.035 M in a solvent comprising about 74% propylene carbonate, about 25% cyanoethyl sucrose and about 1% glacial acetic acid.

The cell gap for these four systems, respectively, were: Example 16 -- about 105 μm; Example 17 -- about 125 μm; Example 18 -- about 105 μm; and Example 19 -- about 100 μm. In the mirrors of Examples 16 and 18, we used HWG (about five-eighths wave to about two-thirds wave) ITO-coated glass substrates, whereas in the mirrors of Examples 17 and 19 we used HW glass substrates.

We observed the color uniformity for these mirrors to be excellent, with the mirrors of Examples 16 and 18 exhibiting a bluish green color while the mirrors of Examples 17 and 19 exhibited a bluish purple color. With respect to the mirrors of each of Examples 16 through 19, we noted the bleaching to be uniform.

We made the following observations in connection with Examples 16 through 19 which are illustrated below in Table 2.

Table 2

Example No.	High Reflect-ance %	Low Reflect-ance %	Color 70-20% R (Sec)	Bleach 10-60% R (Sec)
16	80.6	8.0	1.9	3.6
17	80.6 (73.8)*	6.6 (8.4)*	1.6 (1.7)*	3.2 (5.0)*
18	80.7 (79.8)**	8.0 (7.9)**	2.0 (1.9)**	3.5 (3.8)**
19	79.5	5.2	3.7	9.7

* After about 2,500 KJ/m^2 ultraviolet exposure [see SAE J1960] in electrochemichromic cells with an ultraviolet absorbing, scatter-protecting optically clear, resilient, tear resistant polymer interlayer of plasticized polyvinyl butyral lamination [see United States Patent 5,073,012 (Lynam)] at about 70°C for a period of about 1,825 hours.

** After about 700 KJ/m^2 equivalent ultraviolet exposure as per SAE J1960 in electrochemichromic cells without plasticized polyvinyl butyral lamination at about 70°C for a period of about 1,825 hours.

We measured the ultraviolet stability of the mirrors with a weatherometer which employs a xenon lamp and therewith simulates accelerated exposure to solar radiation. We typically subject the mirrors containing the electrochemichromic solutions of the present invention to an ultraviolet exposure of about 2,500 KJ/m^2 for a period of about 1,825 hours at a temperature of about 70°C. To the mirrors of Examples 17 and 18, supra, we chose an ultraviolet exposure of about 2,500 KJ/m^2 and about 700 KJ/m^2, respectively [see SAE J1960]. As the data recorded for the mirrors of Examples 17 and 18 in Table 2 illustrates, exposure to ultraviolet irradiation for about 1,825 hours did not have an appreciable affect in reducing the quality or the response for either mirror. This is so even keeping in mind that the mirror of Example 18 contained an ultraviolet stabilizing agent, whereas the mirror of Example 17 did not.

RMPT Examples

Example 20

A. Synthesis and Isolation of RMPT

In Example 20, we placed about 2 grams of MPT as synthesized in Example 15(A), supra, in about 60 mls of N,N'-dimethylformamide. We commenced stirring of the resulting solution, and added portionwise about 5 grams of sodium hydrosulfite in about 30 mls of water at about room temperature whereupon the reddish-colored solution turned a pale yellowish color almost immediately. We continued to stir the mixture for a period of time of about 5 minutes, and then poured the mixture into about 300 mls of water. We isolated the product by immediately filtering therefrom the resulting white precipitate. We then dried this precipitate under vacuum to obtain about a 90% yield. We measured the melting point of the product to be about 235°C to about 239°C. Elemental analysis provided the following results: Theoretical: C, 68.1; H, 4.80: N, 6.11 and S, 14.0. Found: C, 65.44; 4.73; N, 6.23 H, and S, 12.77.

B. Use of RMPT in Mirrors

We placed into a mirror, assembled according to Example 1 [except that the cell gap was about 125 μm], an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of EV-ClO_4 (as the cathodic compound) and about 0.02 M of RMPT (as the anodic compound), both dissolved in a solvent comprising propylene carbonate.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror decreased from about 80.8% to about 6.6%, with a changed reflectance of about 70% to about 20% in a response time of about 1.7 seconds when a potential of about 1.3 volts was applied thereto. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.5 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2.6 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent thermal stability and cycle stability.

Examples 21 and 22

We repeated Example 20(B) using the same concentrations of anodic compound and cathodic compound, but in different solvent systems. That is, in Example 21, we employed a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v), and, in Example 22, a solvent comprising about 75% 3-hydroxypropionitrile and about 25% glutaronitrile (v/v). We observed the color uniformity to be excellent with a bluish purple colored appearance. We observed the bleaching to be uniform, and the bleached appearance to be silvery. And, we made the following observations in connection with Examples 21 and 22 which are illustrated below in Table 3.

Table 3

Example No.	High Reflectance %	Low Reflectance %	Color 70-20% R (Sec)	Bleach 10-60% R (Sec)	Bleach 20-60% R (Sec)
21	80.9	6.3	1.6	4.0	2.9
22	80.0	5.9	1.7	4.3	3.1

A comparison of the data obtained in Examples 20, 21 and 22 evidences that RMPT demonstrated comparable results in the presence or absence of an acidic solvent component, and that this anodic compound is electrochemically compatible with a cathodic compound, such as a viologen, in the electrochemichromic solutions of the present invention.

RMPT-DMPA Examples

We have discovered that combining the anodic compounds as described herein -- e.g., RMPT -- with anodic compounds that do not require a redox pre-treatment to render them useful in this connection -- e.g., DMPA -- produces distinguishable colormetric affects in the electrochemichromic devices in which they are placed. Such affects present utility in specific applications where it is desirable for an electrochemichromic device to possess a particular color in the low transmitting, dimmed state. Examples of such an application are architectural windows and rearview mirrors. Examples 23 through 25, infra, illustrate this property employing combinations of RMPT and DMPA.

Example 23

We placed into a mirror, assembled according to Example 1 [except that we used tin oxide coated glass substrates ("TEC-Glass" product of 20 ohms per square sheet resistance supplied as "TEC 20" by Libbey-Owens-Ford Co.) having a cell gap of about 100 μm], an electrochemichromic solution prepared according to the present invention comprising about 0.050 M of $EVClO_4$ (as the cathodic compound) and a combination of about 0.017 M of DMPA and about 0.033 M of RMPT (in combination as anodic compounds), both the cathodic compound and anodic compounds were dissolved in a solvent comprising 3-hydroxypropionitrile.

In connection with the MPT reduction to form RMPT, we followed the reduction and isolation procedure as described in Example 20(A), supra.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly initially to a grayish green color and ultimately to a gray color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 68.1% reflectance which decreased to a low reflectance of about 9.1% when a potential of about 1.3 volts was applied thereto. The response time for the reflectance to change from about 60% to about 20% when a potential of

about 1.3 volts was applied thereto was about 1.5 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 5.9 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 3.8 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent thermal stability and cycle stability.

Examples 24 and 25

In Examples 24 and 25, we used HW ITO-coated glass substrates to assemble the mirrors. The cell gap in the mirror of Example 23 was about 125 μm and the cell gap in the mirror of Example 24 was about 100 μm. We varied the proportions of RMPT to DMPA in these examples as follows.

In Example 24, we chose an equivalent combination of those compounds at about 0.02 M as the anodic compounds and about 0.04 M $EVClO_4$ as the cathodic compound to again illustrate those properties. And, in Example 25, we chose a combination of about 0.012 M RMPT and about 0.023 M DMPA as the anodic compounds to be contacted with about 0.035 M $EVClO_4$ as the cathodic compound to yet again illustrate those properties. We observed the color uniformity to be excellent with the mirror of Example 24 demonstrating a dark bluish green colored appearance and the mirror of Example 25 demonstrating a greenish blue colored appearance. We noted the bleaching to be uniform, and the bleached appearance to be silvery. We made the following observations which are illustrated below in Table 4.

Table 4

Example No.	High Reflectance %	Low Reflectance %	Color 70-20% R (Sec)	Bleach 10-60% R (Sec)	Bleach 20-60% R (Sec)
24	68.0	5.9	1.6*	5.3	--
25	72.5	6.5	2.1	3.8	2.8

* Response time measured from a high reflectance of about 60% reflectance to a low reflectance of about 20% reflectance.

POZ Examples

Example 26

A. Synthesis of POZ

We synthesized POZ according to the procedure described in B.A.K. Chibber et al., "Binding of Actinomycin Chromophore Analogues to DNA", Can. J. Chem., 51, 204 (1973) by oxidizing phenoxazine with $FeCl_3$ in a mixture of about 2:1 acetic acid and water.

B. Use of POZ in Mirrors

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.03 M of $EVClO_4$ (as the cathodic compound) and about 0.03 M of reduced POZ (as the anodic compound), both dissolved in a solvent comprising about 99% 3-hydroxypropionitrile and about 1% glacial acetic acid (v/v). To this solvent we had previously added about 5% of "UVINUL 400" (w/v) as an ultraviolet stabilizing agent.

In connection with the POZ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish gray color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 78.0% decreased to a low reflectance of about 5.9%, with a changed reflectance of about 70% to about 20% in a

response time of about 2.6 seconds when a potential of about 1.3 volts was applied thereto we made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 7.2 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 4.8 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent thermal stability and cycle stability.

Examples 27 and 28

In the mirrors of Examples 27 and 28, we maintained the same electrochemichromic compounds as in Example 26 at about a 0.03 M concentration, but varied the solvent composition. For Example 27, we chose a solvent comprising a combination of propylene carbonate and glacial acetic acid in a ratio of about 99:1 (v/v), whereas for Example 28, we chose a solvent comprising a combination of propylene carbonate, 3-hydroxypropionitrile and glacial acetic acid in a ratio of about 79:20:1 (v/v). We observed the color uniformity to be excellent for the mirrors of Examples 27 and 28, with the mirror of Example 27 demonstrating a bluish colored appearance under an applied potential of about 1.0 volt and about 1.3 volts, whereas the mirror of Example 27 demonstrated a bluish green colored appearance at an applied potential of about 1.3 volts and demonstrated a bluish gray colored appearance at an applied potential of about 1.0 volt. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent thermal stability and cycle stability.

We have illustrated our observations in connection with Examples 27 and 28 below in Table 5.

Table 5

Example No.	Applied Potential (volts)	High Reflectance %	Low Reflectance %	Color 70-20% R (Sec)	Bleach 10-60% R (Sec)	Bleach 20-60% R (Sec)
27	1.3	79.4	7.7	1.3	2.7	2.0
	1.0	79.3	16.5	3.1	--	1.8
28	1.3	77.9	6.1	2.6	4.4	3.1
	1.0	77.9	16.2	6.7	--	3.2

PT Examples

Example 29

A. Synthesis of PT

We synthesized PT according to the procedure described in European Patent Application EP 0 115 394 (Merck Frosst Canada).

B. Use of PT in Mirrors

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced PT (as the anodic compound), both dissolved in a solvent comprising about 2% benzoic acid (w/v) dissolved in a combination of propylene carbonate and glacial acetic acid in a ratio of about 99.95% to about 0.05% (v/v).

In connection with the PT reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 81.4% reflectance which decreased to a low reflectance of about 6.7%. The response time for the reflectance to change from about 70% to about 20% was about 1.7 seconds when a potential of about 1.3 volts was applied thereto. We made that determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.8 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2.9 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent thermal stability and cycle stability.

Example 30

In the mirror of Example 30, we again used PT at about a 0.02 M concentration, but we varied the solvent composition. Specifically, we adjusted the solvent composition to one comprising about 1% benzoic acid (w/v) dissolved in a combination of propylene carbonate and glacial acetic acid in a ratio of about 99.9:0.1 (v/v). Based on this adjustment, although we did not observe a measurable change in qualitative data, the quantitative data are illustrated in Table 6 and the differences are readily apparent from a comparison with Example 30.

Table 6

Example No.	High Reflectance %	Low Reflectance %	Color 70-20% R (Sec)	Bleach 10-60% R (Sec)	Bleach 20-60% R (Sec)
29	81.9	6.6	1.9	3.5	2.7

APOZ Example

Example 31

A. Synthesis of APOZ

We synthesized APOZ according to the procedure described in Chibber, supra.

B. Use of APOZ Mirrors

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.04 M of $EVClO_4$ (as the cathodic compound) and about 0.04 M of reduced APOZ (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the APOZ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a gray color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 76.3% reflectance which decreased to a low reflectance of about 7.0% The response time for the reflectance to change from about 70% to about 20% was about 1.9 seconds when a potential of about 1.0 volt was applied thereto. We made this determination by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.2 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2.3 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be clear indicating acceptable electrochromic performance.

BPOZ Example

Example 32

A. Synthesis of BPOZ

We synthesized BPOZ according to the procedure described in A. Butenandt et al., "Modellversuche zur Konstitution der Ommochrome die Kondensation von Hydroxy-chinonen mit o-Aminophenolen", Liebigs Ann. Chem., 632, 134-43 (1960).

B. Use of BPOZ in Mirrors

We placed into the mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.025 M of $EVClO_4$ (as the cathodic compound) and about 0.025 M of reduced BPOZ (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the BPOZ reduction, we followed the procedure described in Example 1, supra.

Initally, we introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a grayish color with a negligible Iris. We then introduced an applied potential of about 1.3 volts and again observed a rapid and uniform gray color formation.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.5% reflectance which decreased to a low reflectance of about 8.2%. The response time for the reflectance to change from about 70% to about 20% was about 1.6 seconds when a potential of about 1.0 volt was applied thereto. We made this determination by the reflectometer described in Example 1, supra. We then observed that the high reflectance at the center portion of the mirror decreased from about 80.5% to about 6.3% in a response time of about 1.7 seconds when a potential of about 1.3 volts was applied thereto.

We also observed that the mirror, after introducing an applied potential of about 1.3 volts thereto, bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.6 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2 seconds under about zero applied potential. We observed that the mirror, after introducing an applied potential of about 1.0 volt thereto, bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.7 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2.8 seconds under about zero applied potential. We noted that in both instances the mirror bleached uniformly, and the bleached appearance had a yellowish color.

We measured the ultraviolet stability to be very good, and the thermal stability and cycle stability to be excellent.

BMPT Example

Example 33

A. Synthesis of BMPT

We synthesized BMPT according to the procedure described in European Patent application EP 0 115 394 (Merck Frosst Canada). That is, we dissolved about 2 grams of 2-bromo-6-methyl-1,4-benzoquinone in about 40 mls of methanol, and added thereto over a period of about 20 minutes a solution of about 0.7 grams of 2-amino-thiophenol in about 10 mls of methanol. Once the addition was complete, we allowed the mixture to continue to stir at about room temperature for a period of about 2 hours. We then isolated the product by filtering off the brownish-red precipitate and washing this precipitate with methanol. We obtained a greater than about 60% yield. We measured the melting point of the product to be from about 176 °C to about 178 °C.

B. Use of BMPT in Mirrors

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced BMPT (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the BMPT reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.3 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 81.4% reflectance which decreased to a low reflectance of about 6.6% when potential of about 1.3 volts was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 2.4 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.8 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 2.8 seconds under about zero applied potential. We noted bleaching to be uniform, and the bleached appearance to be silvery. We observed the cycle stability over about 15,000 15-15 second color-

bleach cycles to be excellent under an applied potential of about 1.0 volt to color and about zero volts to bleach.

KEPA Example

Example 34

A. Synthesis of KEPA

We synthesized KEPA according to the procedure described in H. McIlwain, "The Phenazine Series. Part IV. Reactions of Alkyl Phenazonium Salts; the Phenoxyls", J. Chem. Soc., 1704-11 (1937).

B. Use of KEPA in Mirrors

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of EV-ClO_4 (as the cathodic compound) and about 0.02 M of reduced KEPA (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the KEPA reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 68.0% reflectance which decreased to a low reflectance of about 6.3% when a potential of about 1.0 volt was applied thereto. The response time for reflectance to change from about 60% to about 20% was about 1.6 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 6.1 seconds, and from about 20% reflectance to about 60% reflectance in a response time of about 4.6 seconds under about zero applied potential. We noted bleaching to be uniform, and the bleached appearance to be silvery. We observed the cycle stability over about 2,000 15-15 second color-bleach cycles to be good under an applied potential of about 1.4 volts to color and about zero volts to bleach.

DCI Example

Example 35

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 125 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.03 M of $EVCLO_4$ (as the cathodic compound) and about 0.03 M of reduced DCI (as the anodic compound), both dissolved in a solvent comprising about 99% propylene carbonate and about 1% glacial acetic acid (v/v).

In connection with the DCI reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.4 volts to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 78.6% which decreased to a low reflectance of about 7.3% when a potential of about 1.4 volts was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 3.6 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.7 seconds under about zero applied potential. We noted the bleaching to be uniform, and the bleached appearance to be silvery indicating excellent electrochromic performance.

AA Example

Example 36

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced AA (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the AA reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.0% reflectance which decreased to a low reflectance of about 7.1% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.1 seconds, as determined by the reflectometer described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.4 seconds under about zero applied potential. We noted the bleaching to be uniform.

AB Example

Example 37

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced AB (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the AB reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 79.5% reflectance which decreased to a low reflectance of about 6.8% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.2 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.8 seconds under about zero applied potential. We noted the bleaching to be uniform.

AC Example

Example 38

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced AC (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the AC reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.6% reflectance which decreased to a low reflectance of about 8.3% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.1 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 5.1 seconds under about zero applied potential. We noted the bleaching to be uniform.

MB Example

Example 39

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced MB (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the MB reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 81.1% reflectance which decreased to a low reflectance of about 9.0% when a potential of about 1.0 volt was applied

thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.5 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.6 seconds under about zero applied potential. We noted the bleaching to be uniform.

Thionin Examples

Examples 40 (THCl)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin chloride ("THCl") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the THCl reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a bluish purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.4% reflectance which decreased to a low reflectance of about 6.8% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.2 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 3.5 seconds under about zero applied potential. We noted the bleaching to be uniform.

Example 41 (THAc)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin acetate ("THAc") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the THAc reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 81.8% reflectance which decreased to a low reflectance of about 6.8% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.2 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 4.2 seconds under about zero applied potential. We noted the bleaching to be uniform.

Example 42 ($THClO_4$)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin perchlorate ("$THClO_4$") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the $THClO_4$ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 79.4% reflectance which decreased to a low reflectance of about 9.2% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.5 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 6.1 seconds under about zero applied potential. We noted the bleaching to be uniform.

Example 43 ($THBF_4$)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to this invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin tetrafluoroborate ("$THBF_4$") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the $THBF_4$ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.6% reflectance which decreased to a low reflectance of about 9.4% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.6 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 10% reflectance to about 60% reflectance in a response time of about 5.7 seconds under about zero applied potential. We noted the bleaching to be uniform.

Example 44 ($THPF_6$)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin hexafluorophosphate ("$THPF_6$") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the $THPF_6$ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.2% reflectance which decreased to a low reflectance of about 11.7% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.8 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 20% reflectance to about 60% reflectance in a response time of about 3.5 seconds under about zero applied potential. We noted the bleaching to be uniform.

Example 45 ($THCF_3SO_3$)

We placed into a mirror, assembled according to Example 1 (except that the cell had a gap of about 135 μm), an electrochemichromic solution prepared according to the present invention comprising about 0.02 M of $EVClO_4$ (as the cathodic compound) and about 0.02 M of reduced Thionin trifluorosulfonate ("$THCF_3SO_3$") (as the anodic compound), both dissolved in a solvent comprising about 99.5% propylene carbonate and about 0.5% glacial acetic acid (v/v).

In connection with the $THCF_3SO_3$ reduction, we followed the procedure described in Example 1, supra.

We introduced an applied potential of about 1.0 volt to the filled mirror and thereafter observed that the mirror colored rapidly and uniformly to a purple color with a negligible Iris.

In addition, we observed that the high reflectance at the center portion of the mirror was about 80.4% reflectance which decreased to a low reflectance of about 11.7% when a potential of about 1.0 volt was applied thereto. The response time for the reflectance to change from about 70% to about 20% was about 1.6 seconds, as determined by the reflectometer as described in Example 1, supra.

We also observed that the mirror bleached from about 20% reflectance to about 60% reflectance in a response time of about 2.8 seconds under about zero applied potential. We observed the bleaching to be uniform.

In general, we have found superior electrochromic performance in accelerated ultraviolet testing for di-amino phenothiazine derivatives which have primary (1°) or secondary (2°) amino substituents, such as AC and THAc, as compared to those di-amino phenothiazine derivatives which have at least one tertiary (3°) amino substituent, such as AA, AB and MB.

While we have provided the above examples for illustrative purposes employing preferred electrochemichromic compounds and solvents, it is to be understood that each of the electrochemichromic compounds and solvents identified herein will provide suitable, if not comparable, results when viewed in connection with the results gleaned from these examples.

Although we have described the foregoing invention in some detail by way of illustration and example, it will be clear to one of ordinary skill in the art that changes and modifications may be practiced within the spirit of the claims which define the scope of the present invention. Thus, the art-skilled will recognize or readily ascertain using no more than routine experimentation, that equivalents exist to the embodiments of the invention described herein. And, it is intended that such equivalents be encompassed by the claims which follow hereinafter.

Claims

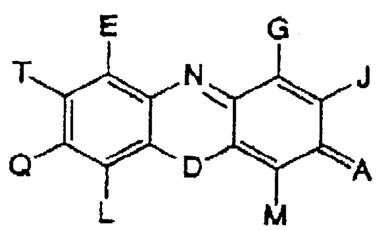
1. An electrochemichromic solution capable of color change when an applied potential is introduced thereto, said electrochemichromic solution comprising:

(a) at least one anodic compound, said anodic compound having been previously contacted with a redox agent such that said anodic compound exists in a different valence state than prior to having been contacted with said redox agent;
(b) at least one cathodic compound; and
(c) a solvent

wherein the redox potential of said at least one anodic compound in said different valence state is greater than the redox potential of said at least one cathodic compound while contacted with said solvent.

2. The electrochemichromic solution according to claim 1, wherein said at least one anodic compound is a combination of two or more anodic compounds, wherein at least one of said at least one anodic compound in said combination need not be pre-contacted with said redox agent.

3. The electrochemichromic solution according to claim 1, wherein said anodic compound is represented by the formula below:



wherein A is O, S or NRR_1;

wherein R and R_1 may be the same or different and each may be selected from the group consisting of H or any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms, provided that when A is NRR_1, Q is H, OH or NRR_1;

D is O, S, NR_1 or Se;

E is R_1, COOH or $CONH_2$;

G is H;

J is H, any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms, NRR_1,

$$NR\overset{\overset{\displaystyle O}{\|}}{C}R_1,$$

OR_1, phenyl, 2,4-dihydroxyphenyl or any halogen; or G and J, taken together, represent an aromatic ring structure having six carbon ring atoms when viewed in conjunction with the ring carbon atoms to which they are attached;

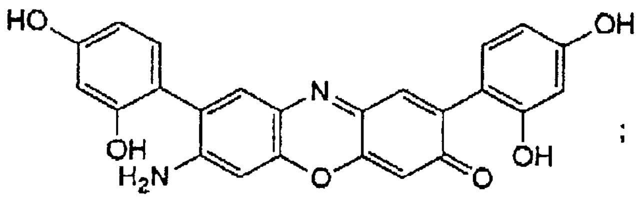
L is H or OH;

M is H or any halogen;

T is R_1, phenyl or 2,4-dihydroxyphenyl; and

Q is H, OH or NRR_1.

4. The electrochemichromic solution according to claim 3, wherein said anodic compound is a member selected from the class of chemical compounds consisting of the following formulae: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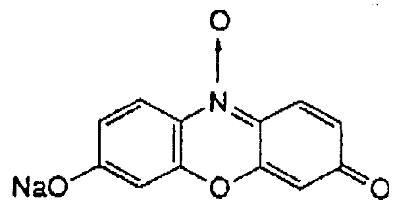
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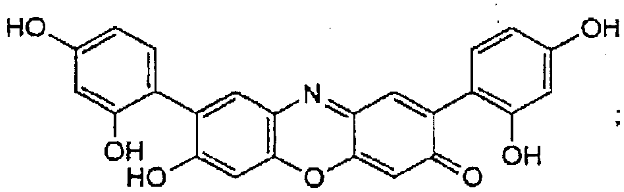
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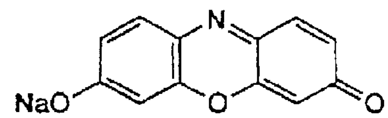
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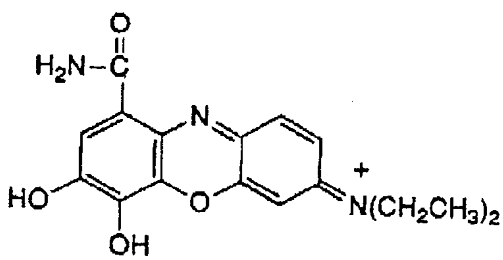
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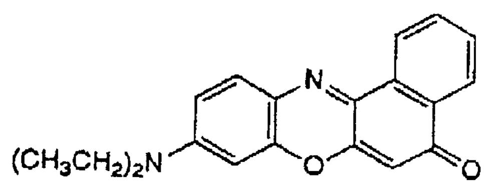
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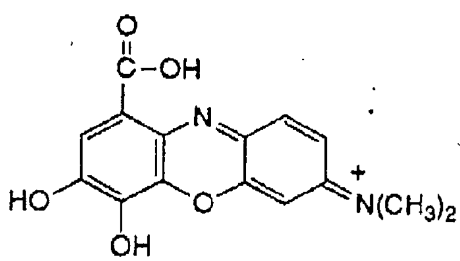
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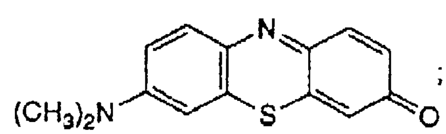
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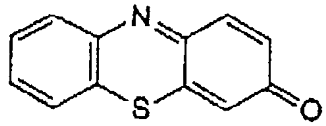
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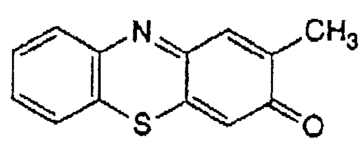
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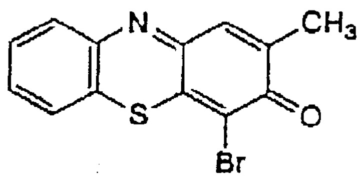
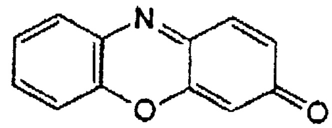
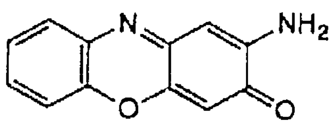
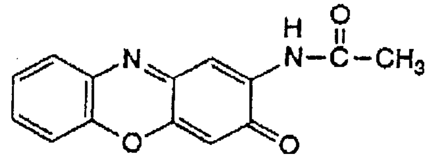
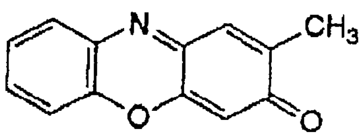
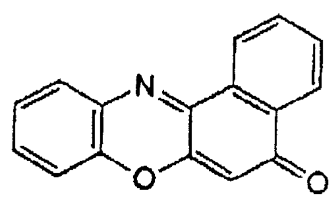
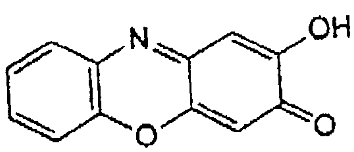
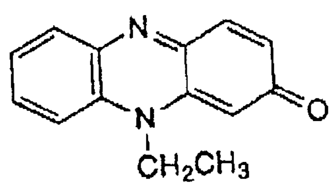
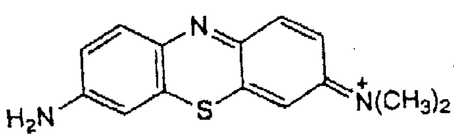
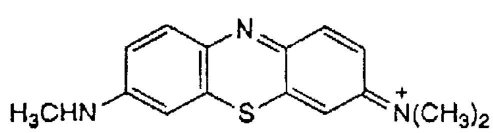
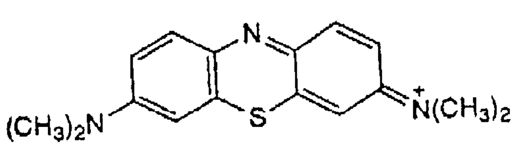
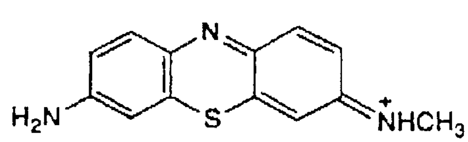
 ;  ;

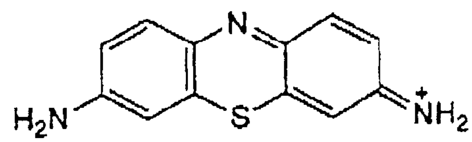
 ;  ;

 ;  ;

 ;  ;

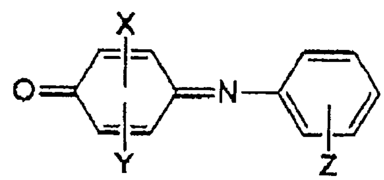
 ;  ;

 ;  ;



5. The electrochemichromic solution according to claim 1, wherein said at least one anodic compound has been isolated after having been contacted with said redox agent.

6. The electrochemichromic solution according to claim 1, wherein said anodic compound is represented by the formula below:

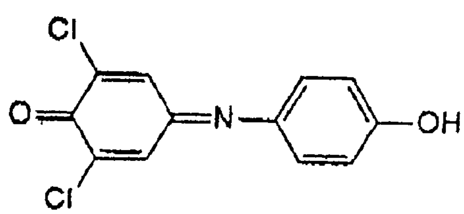


wherein

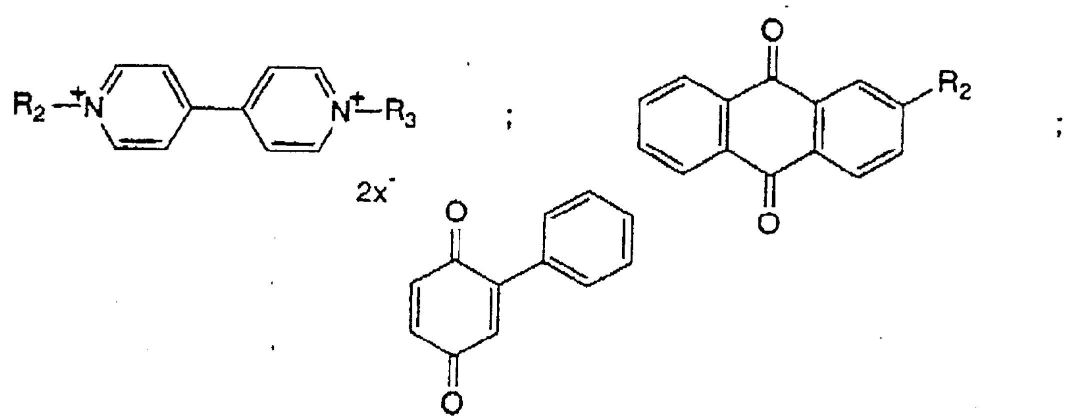
X and Y may be the same or different and each may be selected from the group consisting of H, any halogen and NRR_1, wherein R and R_1 may be the same or different and each may be selected from the group consisting of H or any straight- or branched-chain alkyl constituent having from about one carbon atom to about three carbon atoms; or, X and Y, taken together, represent an aromatic ring structure having six carbon ring atoms when viewed in conjunction with the ring carbon atoms to which they are attached; and

Z is OH or NRR_1, or salts thereof.

7. The electrochemichromic solution according to claim 6, wherein said anodic compound is



8. The electrochemichromic solution according to claim 1, wherein said cathodic compound is selected from the group of chemical compounds consisting of the following formulae:



wherein

R_2 and R_3 may be the same or different and each may be selected from the group consisting of H, any straight- or branched-chain alkyl constituent having from about one carbon atom to about six carbon atoms, or any straight-or branched-chain alkyl- or alkoxy-plenyl, wherein said alkyl or alkoxy constituent contains from about one carbon atom to about six carbon atoms;

X is selected from the group consisting of tetrafluoroborate, perchlorate, trifluoromethane sulfonate, hexafluorophosphate, any halide and combinations thereof.

9. The electrochemichromic solution according to claim 1, wherein said redox agent of (a) is a reducing agent capable of causing an electrochemichromic composed to assume a decreased valence state upon contacting therewith as compared with that valence state possessed by said electrochemichromic compound prior to having been contacted with said reducing agent.

10. The electrochemichromic solution according to claim 1, wherein said solvent of (c) is a member selected from the group consisting of acetonitrile, 3-hydroxypropionitrile, methoxypropionitrile, 3-ethoxypropionitrile, propylene carbonate, 2-acetylbutyrolactone, cyanoethyl sucrose, γ-butyrolactone, 2-methylglutaronitrile, N,N'-dimethylformamide, 3-methylsulfolane, methylethyl ketone, cyclopentanone, cyclohexanone, benzoyl acetone, 4-hydroxy-4-methyl-2-pentanone, acetophenone, glutaronitrile, 3,3'-oxydipropionitrile, 2-methoxyethyl ether, triethylene glycol dimethyl ether and combinations thereof.

11. The electrochemichromic solution according to claim 1, wherein said solvent of (c) is acidic.

12. The electrochemichromic solution according to claim 10, wherein said solvent is rendered acidic by employing as a solvent component an acidic material selected from the group consisting of acetic acid, any hydrogen halide gas in solution, perchloric acid, 2-acetylbutyrolactone, 3-hydroxypropionitrile, benzoic acid in solution, ascorbic acid in solution and combinations thereof.

13. The electrochemichromic solution according to claim 10, wherein said solvent component is acetic acid employed in the range of about 0.5% (v/v) to about 5% (v/v).

14. An electrochemichromic compound capable of undergoing a reversible color change when its valence state is altered due to oxidation, wherein said composed is a member selected from the group consisting of methylene violet (Bernthsen), 2-methyl-phenothiazin-3-one, phenothiazin-3-one and phenoxazin-3-one.

15. A process for preparing an anodic compound, said process comprising the steps of:

(a) solubilizing an electrochemichromic compound in a solvent; and

(b) contacting said solubilized electrochemichromic compound with a redox agent to alter the valence state of said electrochemichromic compound such that an anodic compound is created in solution which has a different valence state than said solubilized electrochemichromic compound possessed prior to having been contacted with said redox agent.

16. The process according to claim 15, further comprising the step of:

(c) isolating said anodic compound.

17. The process according to claim 15 or 16, wherein said electrochemichromic compound is a member selected from the group consisting of methylene violet (Bernthsen), 2-methyl-phenothiazin-3-one, phenothiazin-3-one and phenoxazin-3-one.

18. The anodic compound prepared by the process according to claim 15 or 16.

19. A process for preparing the electrochemichromic solution according to any one of claims 1 through 13, said process comprising the steps of:
(a) solubilizing an electrochemichromic compound with a solvent;
(b) contacting said solubilized electrochemichromic compound with a redox agent to alter the valence state of said electrochemichromic compound such that an anodic compound is created in solution which has a different valence state than said solubilized electrochemichromic compound possessed prior to having been contacted with said redox agent;
(c) contacting said anodic compound with a cathodic compound to form said electrochemichromic solution; and
(d) introducing an applied potential to said electrochemichromic solution such that a current passes through said electrochemichromic solution thereby causing a color change thereof.

20. The process according to claim 19, further comprising after step (b) the step of:
(i) isolating said anodic compound.

21. A process for using an electrochemichromic solution according to any one of claims 1 through 13, said process comprising the steps of:
(a) inserting said electrochemichromic solution into a cell;
(b) sealing said cell so that said electrochemichromic solution is prevented from escaping therefrom; and
(c) introducing an applied potential to said electrochemichromic solution contained in said cell such that a current passes therethrough to cause a color change thereof.

22. An electrochemichromic device comprising:
(a) a first substantially transparent substrate coated with a substantially transparent conductive coating on its interior face;
(b) a second substantially transparent substrate coatad with a substantially transparent conductive coating on its interior face, said second substrate positioned in substantially parallel spaced-apart relationship with said first substrate and being laterally displaced therefrom;
(c) a sealing means positioned toward the peripheral edge of each of said first substrate and said second substrate and sealingly forming a cell cavity therebetween;
(d) the electrochemichromic solution according to any one of claims 1 through 13 having been dispensed into and confined within said cell cavity; and
(e) a means for introducing an applied potential to said electrochemichromic solution to controllably cause a variation in the amount of light transmitted through said device.

23. The electrochemichromic device according to claim 22, wherein said transparent conductive coating may be constructed from a material selected from the group consisting of indium tin oxide, indium tin oxide full wave, indium tin oxide half wave, indium tin oxide half wave green, tin oxide, antimony-doped tin oxide; fluorine-doped tin oxide, antimony-doped zinc oxide and aluminum-doped zinc oxide.

24. An electrochemichromic device comprising:
(a) a first glass substrate coated with a conductive coating on its interior face;
(b) a second glass substrate coated with a conductive coating on its interior face, said second glass substrate positioned in substantially parallel spaced-apart relationship with said first glass substrate;
(c) a sealing means positioned toward, but inward from, the peripheral edge of each of said first substrate and said second substrate and sealingly forming a cell cavity therebetween;
(d) an electrochemichromic solution capable of color change when an applied potential is introduced thereto, said electrochemichromic solution comprising:
(1) an electrochemichromic compound selected from the group consisting of methylene violet (Bernthsen), 2-methyl-phenothiazin-3-one, phenothiazin-3-one and phenoxazin-3-one, wherein

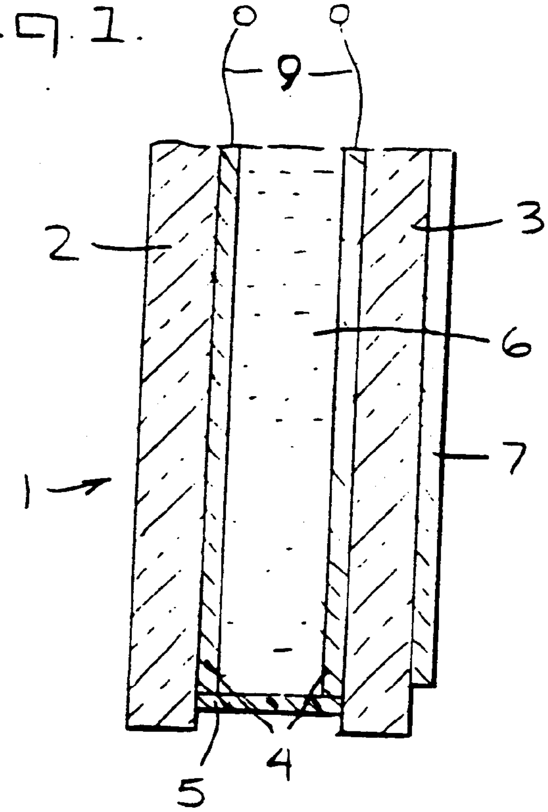
said compound has previously been reduced;
(2) a viologen salt; and
(3) a solvent, wherein said solvent is a member selected from the group consisting of the combination of 3-hydroxypropionitrile, glutraronitrile and acetic acid, the combination of propylene carbonate and acetic acid, the combination of 3-ethoxypropionitrile and 2-acetylbutyrolactone, the combination of 3-ethoxypropionitrile, glutaronitrile and acetic acid, the combination of 3-hydroxypropionitrile, 3,3′-oxydipropionitrile and acetic acid, and the combination of propylene carbonate, cyanoethyl sucrose and acetic acid, wherein said solution has been dispensed into and confined within said cell cavity; and
(e) a means for introducing an applied potential to said electrochemichromic solution to controllably cause a variation in the amount of light transmitted through said solution.

25. The electrochemichromic device of claim 24, further comprising after (d) (1):
(i) said previously reduced electrochemichromic compound having thereafter been isolated.

26. The electrochemichromic device according to any one of claims 22 through 25, wherein said device is selected from the group consisting of mirrors, glazings, partitions, filters, displays and lenses.

27. The electrochemichromic device according to claim 26, wherein said device is a mirror further comprising a reflective coating on a face of said second glass substrate.

Fig. 1.



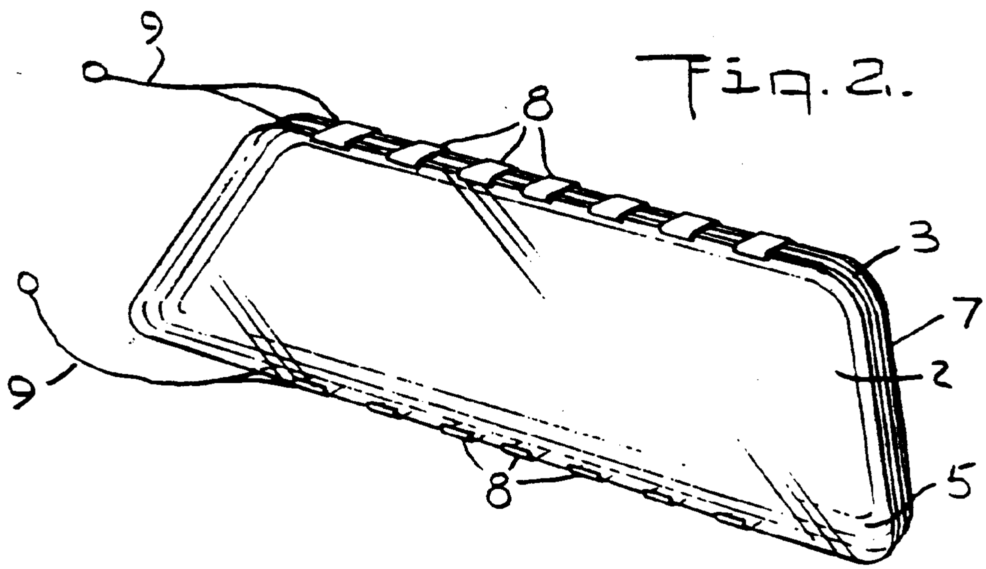


Fig. 2.